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**(54) DEORORIZING FIBER, PROCESS FOR PREPARING THE SAME, AND DEODORIZING FIBER PRODUCT**

(57) Described is a deodorizing fiber having an acid group in the fiber substrate of the fiber in a proportionate amount of 0.01 - 2.5 mol/kg fiber and an amino group containing compound in a proportionate amount of 0.03 - 3 mol/kg fiber and the amino group containing compound being chemically bonded in the fiber between the acid group and at least a part of the amino group contained in the amino group containing compound.

The acid group can be carboxyl group and/or sulfonic acid group. A preferred amino group containing compound is a water soluble polyimine having a molecular weight of 1,000 - 200,000.

The fiber of the invention is preferably prepared by impregnating or immersing a never-dried wet spun acrylic fiber with an aqueous solution of a water soluble polyamine, and heat treating the impregnated fiber at a temperature between 100 and 180°C. A textile article made from the deodorizing fiber of the invention in combination with a deodorizing fiber having an anionic functional group can remove an objectionable compound smell or odor in the ambient atmosphere.

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## Description

### Field of the Invention

5 This invention relates to a deodorizing fiber having a characteristic of removing unpleasant or offensive smells (or odors) perceptible in dwelling houses and accommodation. This invention relates to deodorizing textile articles capable of removing a broad range of smells or odors.

### Background Art

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In recent years, comfortable living environments have become the object of attention. There have been known many attempts for removing offensive smells present in various environments, for examples, in a living room, in a vehicle and even in a refrigerator.

15 Among the attempts, special attention has been focused on deodorizing tobacco smoke smells present in an office, in a living room and in automobile on account of the penetration of anti-smoking movement.

Some deodorants utilizing amine compounds for removing tobacco smoke smells have already been proposed. For example, an acrylic woven fabric containing a deodorant carrying a polyethylene-imine and nonionic moisture absorbing organic substances has been disclosed in Japanese Unexamined Patent Publication (Kokai) No. 3-146064.

20 However, it has been found that the proposed fabric does not provide a satisfactory characteristics pertaining to durability to washing and to processability.

A material for a tobacco smoke filter in which a reactive group is introduced into a cellulosic molecule to be reacted with a polyethylene-imine is disclosed in Japanese Unexamined Patent Publication (Kokai) No. 57-16687. The proposed product produces a localized formation of bonded reacted polyethylene-imine and the bonded polyethylene-imine is readily stripped off.

25 Further more, Japanese Unexamined Patent Publication (Kokai) No. 62-141128 describes a deodorizing synthetic acrylic fiber and a process for producing the same in which an amino group-introduced metal porphyrin was incorporated in the wet-gel fiber (undried fiber) in a manufacturing process stage of an acrylic fiber in order to improve fastness to washing, and the fiber was subsequently dried to produce a deodorizing densified fiber. Although the deodorizing characteristics of the synthetic acrylic fiber according to the proposed method exhibits a satisfactory fastness to washing, the fiber is not durable to dyeing. In the patent publication, it is described that a polyvinyl amine which is a polyamine is chemically bonded to metal porphyrin. In this case, since the polyvinyl amine and the metal form a water-insoluble complex-compound, it is hardly possible to apply the compound in the form of a solution to a fiber because the polyvinyl amine and the metal form an complex which is insoluble in water. It is natural that the complex adheres only to surface of fiber. Accordingly, the resultant textile products lacks fastness to dyeing.

35 As methods for improving dyeability, chemical incorporation of an amine compound to a fiber substrate has been known in the art. The methods include, for example, copolymerization of fiber forming polymer (Japanese Examined Patent Publications (Kokoku) No. 47-15096, No. 47-32157, No. 48-30479 and No. 55-6725), application of graft polymerization to as-spun fiber after fiber forming process (Japanese Patent Publication (Kokoku) No. 38-8218, No. 47-23988 and No. 37-15415), polymer blending technique (Japanese Patent Publications (Kokoku) No. 38-20972 and No. 37-2997), direct application of impregnation method to fiber (Japanese Examined Patent Publications (Kokoku) No. 29-8215, No. 47-23988 and No. 48-23834) and the like.

40 In any of these known methods, amine compounds incorporated in fibers are preferably in the form of a salt according to the descriptions of publications. The fibers according to these known methods lack the capability of deodorizing offensive smells from an acid compound and/or a compound containing carbonyl groups which is a source of an offensive smell.

45 Japanese Examined Patent Publication (Kokoku) No. 22673 describes a cleaning filter in which a plurality of carrier substrates each impregnated with different components capable of deodorizing a plurality of different kinds of unpleasant smells are compounded. Textile articles in which a carried deodorant is adhered to the surface of a fiber by coating or impregnation, feel stiff to the hand. Since the deodorant component is readily stripped off when the articles are washed or dyed, these textile articles cannot be used for clothing, interiors and furnishings where fastness to washing and dyeing or fashionable qualities are required.

50 In a textile article using a deodorizing fiber, it is generally required that the deodorizing characteristics of the fiber should be fast or durable against washing and dyeing processes. With a view extending the end-use field of a deodorizing fiber, dyeing of deodorizing fiber is strongly required as in conventional fibers. The deodorizing characteristics of deodorizing fiber should be retained even after the fiber has been dyed. In other words, durability of deodorizing characteristics to dyeing property is extremely important requirement in a dyed deodorizing fiber.

55 The fastness to washing referred to herein is defined as a retention degree (preservation degree) of the original characteristics of a textile article after washing in which a deposit adhered to the fiber prior of washing has been

stripped off (removed) by both mechanical and chemical actions of flowing washing water in the presence of a minimum surfactant which does not deteriorate physical characteristics and does not change the color of the textile article. Washing is a treatment applied to with a view to stripping off the deposit or the adherent which is generally bonded by means of physical adsorption (Washing Test Method is described in JIS-L-0217.).

On the other hand, the fastness to dyeing as herein referred to is defined as a retention degree of the original characteristics of a fiber after dyeing in which a deposit adhered to the fiber prior to dyeing has been stripped off (removed) under heat at dyeing by a strong thermodynamic action, and the property indicates an occurrence of stripping-off of physically adsorbed deposit and ionically bonded adduct. Retention of deodorizing characteristics towards unpleasant smells after the deodorizing fiber has been dyed has been a very serious problems to deal with.

#### Disclosure of the Invention

The object of the present invention is, in a broad sense, to provide a deodorizing fiber and a textile article with durable deodorizing characteristic.

A specific object of the invention is to provide a deodorizing fiber and textile article with deodorizing characteristics exceedingly durable against various treatments, for example, washing and dyeing to which a conventional fiber or textile article is subjected.

A more specific object of the invention is to provide a fiber material having excellent deodorizing characteristics which will not be lost under routine treatments applied during use.

A further object of the invention is to provide durable textile articles exhibiting deodorizing effect on a broad spectrum of unpleasant smells.

This invention provides, in the broadest sense, a deodorizing fiber characterized in that the fiber contains an acid group in the fiber substrate in a proportionate (proportional) amount of 0.01 - 2.5 mol/kg fiber, and carries an amino group-containing compound in a proportionate amount of 0.03 - 3 mole/kg fiber in terms of the amino group thereof which is held by at least part of the amino group bonded chemically to the acid group in the fiber substrate.

The acid group as herein referred to is the acid group contained inherently in the substrate forming fiber, for example, a carboxyl group or sulfonic group which can be reacted with the amino group containing compound.

The fiber pertaining to the invention is an organic fiber and includes natural fibers, chemical fibers and synthetic organic fibers. Representative examples for natural fibers are cotton and wool. The chemical fibers include regenerated cellulose fibers such as viscose rayon, cuprammonium rayon and a fiber formed by means of chemical modification of natural cellulosic materials, for example, acetate fiber. The synthetic organic fibers are made from fiber forming organic synthetic polymers. Representative examples of the fibers are polyamide fiber, acrylic fiber, polyester fiber, or the like.

In the case where these fibers do not have any acid group in themselves, a modifying compound having an acid group is incorporated or introduced into the fibers by means of addition bonding or alternatively they can be used as substrate fiber after they have been treated with a suitable modifier to make a fiber containing a prescribed amount of an acid group.

In the case where the fibers are synthetic organic polymeric fibers, the acid group is introduced during the preparation of the polymer by means of copolymerizing a prescribed amount of a copolymerizable monomer, and a fiber containing the acid group in a proportionate amount of 0.01 - 2.5 mole/kg fiber can be easily prepared by applying a known spinning and stretching process to the obtained copolymer.

In the invention, acrylic fiber can be used as the most preferred fiber substrate for the purpose because the fiber is made from copolymer containing a prescribed amount of an acid group which can be readily prepared in the manner as mentioned above.

In the invention, the amino group is a salt-unsubstituted amino group of which introduction into the fiber is made by chemically bonding a polyamine having a molecular weight of 1,000 - 200,000 with fiber and held firmly on the fiber. The salt-substituted amino group is a neutralized amine by an acid, for example, an amino sulfate and a chloride of amino hydrochloric acid. It cannot absorb smells emitted from a carbonyl group-containing compound and an acid compound up to a satisfactory level, and cannot make a fiber having a fast deodorizing effect.

The deodorizing fiber according to the invention has an amino group bonded firmly on the fiber in which the amino group is chemically bonded to 50 - 100 mol%, preferably 60 mole% or more of the acid group contained in the fiber. Since the deodorizing fiber of the invention carries a sufficient amount of amino group bonded chemically to the acid group in the fiber substrate, a remarkable removal of unpleasant acid smells emitted from aldehyde and sulfide can be effected and the deodorizing characteristics of the fiber becomes durable against physico-chemical actions encountered during dyeing and washing.

It is, however, noted that a deodorizing effect cannot be attained in case where an amount of amino group present in the fiber is relatively small as compared with a relatively larger amount of acid group present in the fiber substrate. Accordingly, an application of greater amount of amino group is required so as to maintain the presence of a free amino group in the fiber because the free amino group effects deodorizing.

The deodorizing fiber according to the invention can be prepared by a process comprising contacting a raw material fiber containing an acid group in the fiber substrate in a proportionate amount, as mentioned above with an aqueous solution of a water-soluble polyamine, especially a water-soluble polyamine having a molecular weight of 1,000 - 200,000 containing 0.025 mol/kg solution based on a molar amount of an acid group as mentioned above to obtain a fiber impregnated with polyamine; heat treating the impregnated fiber with the water soluble polyamine in an ambient temperature of 100°C or more.

In the process, the concentration of a treating or immersing bath of the water soluble polyamine can be optionally selected as far as the prescribed amount of water soluble polyamine compound can be attached to the fiber. The amount of water-soluble polyamine compound attached to the fiber can be determined on the basis of a pick up ratio or a squeezed solution ratio.

When the heat treatment is carried out under moist or wet heat or steam, the deodorizing characteristics of fiber becomes fast to dyeing and washing. When the deodorizing fiber is an acrylic fiber, deodorizing fastness of the fiber to treatments such as washing and dyeing can be further enhanced by a process comprising impregnating a never-dried fiber (hereinafter, the fiber may be referred to as undried fiber.) with a polyamine compound in which the never-dried fiber is a fiber immediately after stretching in forming an acrylic fiber in a wet spinning or gap-type wet spinning process.

The deodorizing fiber of the invention can be of either continuous fiber or staple fiber. When the fiber is chemical or synthetic fiber, it can be prepared in the form of a tow. The deodorizing fiber of the invention may be used in the form of yarn, and it is mostly converted into the form of woven fabric, knitted fabric or nonwoven fabric for making textile articles such as clothing or the like. In the textile goods as mentioned above, goods can be wholly composed of the fiber of the invention. The deodorizing fiber of the invention can be blended with a conventional fiber to make a textile article.

An durable deodorizing textile article which exhibits an extensive deodorizing characteristics capable of effecting extensive removal of compound smells having a wide smell spectrum covering acid compound-based smell and basic compound-based smell, can be attained by blending at least 5% by weight of a deodorizing fiber of the invention with at least 0.5% by weight of a fiber exhibiting a deodorizing characteristic towards a basic compound-based smell, especially a fiber containing an anionic functional group at a content of 0.2 - 10 mol/kg fiber or else a deodorizing fiber containing a transition metal at a content of less than 0.1 - 5 mol/kg fiber bonded to the anionic functional group mentioned above.

The anionic functional group contained in the fiber enabling to deodorize the basic compound-based smell as referred to herein, is a sulfonic group or carboxyl group which can be introduced into the fiber substrate of natural fibers, chemical fibers or synthetic fibers by the same method as that method for introducing the acid groups as mentioned-above. A transition metal is introduced into the fiber by contacting the fiber containing the anionic functional group as mentioned-above with an aqueous solution of a metal salt, for examples, a metal sulfate, a metal nitrate, and the like.

The mixed or blended fiber can be made into a final product in the form of a woven or knitted union fabric, a twisted plied yarn, a mixed knitted fabric, nonwoven by application of conventional converting means.

#### Best Mode of Carrying Out of the Invention

An acid group contained in the deodorizing fiber of the invention is preferably carboxyl group or sulfonic group, especially sulfonic group. The deodorizing fiber of the invention contains an acid group at a proportionate content of 0.01 - 2.5 mol/kg fiber, preferably 0.01 - 1.5 mol/kg fiber. When a proportionate content of acid group is less than 0.01 mol/kg fiber, a satisfactory bond between an acid group and a water-soluble polyamine cannot be attained and the water-soluble polyamine having amino group may be readily stripped off from the fiber during dyeing and washing treatment. Accordingly, a proportionate content of less than 0.01 mol/kg fiber for acid group cannot be used in the invention. On the contrary, when a proportionate content of acid group exceeds 2.5 mol/kg fiber, acid group-containing polymeric compound in the fiber become readily detached during dyeing and washing.

When a fiber does not contain an acid group, the acid group can be introduced into the fiber by producing a prescribed amount of carboxyl group in the fiber substrate by means of an addition of a chemical substance to the fiber substrate using a known method such as a graft polymerization, or by means of a chemical modification of the fiber using a chemical treatment such as oxidization. Such means for introducing an acid group can be used as a method for preparation of a fiber containing a prescribed amount of carboxyl group from wool, cotton, a regenerated cellulose fiber and a cellulose acetate fiber.

Introduction of a prescribed amount of an acid group into a synthetic organic fiber can be easily made with use of a copolymer prepared by copolymerizing a comonomer having a prescribed amount of an acid group by applying a known suitable spinning and stretching method for the copolymer.

For both of a condensation polymerized copolymer pertaining to polyamide fibers and polyester fibers and a addition polymerized polymers pertaining to acrylic fibers, preparations of the respective fiber forming polymers containing a prescribed amount of an acid group by an addition of comonomer having carboxyl or sulfonic group can be practiced using a conventionally known method.

Acrylic fibers are suitable fibers for preparation of fiber containing carboxyl or sulfonic group using a copolymerizing method, and are preferable fiber materials capable of providing a deodorizing fiber of the invention with the fiber substrates because the method for forming the fibers from a copolymer having a prescribed amount of carboxyl or sulfonic group as well as the properties of the fibers are not different substantially from a conventional acrylic fiber.

Examples of acrylic synthetic fibers constituting a deodorizing acrylic fiber of the invention are copolymeric fibers obtained by copolymerizing 30% or more by weight of acrylonitrile with one or two or more vinyl monomers including acrylic acid, methyl acrylate, ethyl acrylate, itaconic acid, methacrylic acid, styrene, acryl amide, methacryl amide, vinyl acetate, vinyl chloride, vinylidene chloride, metharyl sulfonic acid, a salt of metharyl sulfonic acid, styrene sulfonic acid, a salt of styrene sulfonic acid, aryl sulfonic acid, a salt of aryl sulfonic acid and the like.

In the invention, especially preferred acrylic fibers are fibers made of copolymers obtained by copolymerizing 80% or more by weight of acrylonitrile with one or two or more of vinyl monomers including acrylic acid, methyl acrylate, methyl methacrylate, acryl amide, vinyl acetate, vinyl chloride, a salt of metharyl sulfonic acid, a salt of styrene sulfonic acid and the like.

It is necessary that a deodorizing fiber of the present invention contains an amino group in a proportionate content of 0.03 - 3.0 mol/kg fiber, preferably 0.05 - 2 mol/kg fiber. When the content becomes less than 0.03 mol/kg fiber, absorption characteristics of the fiber towards unpleasant smells from a carbonyl group-containing compound and an acid compound are lowered. When the content exceeds 3 mol/kg fiber, handling touch of the fiber becomes worse.

It is noted that the amino group in the fiber is fixedly held by the bond between the acid group and polyamine compound having amino group, preferably polyamine compound having a molecular weight of 1,000 - 200,000.

In a deodorizing fiber according to the invention, a selective use of polyamine for introducing amino group is preferably made of a water-soluble polyamine having more than two functional group which is not substituted by salt. Examples of water-soluble polyamine compounds include ethylene diamine, diaminopropyl amine, 2,2'-azo-bis-(2-amizino propane), carbohydrazine, thiocarbohydrazide, thiocarbohydrazide, thiosemihydrozide, thiourea, guanidine salts, guanylurea salts, 1,4-diaminobutane, diaminopropane, diaminomaleonitrile, spiroacetal compounds, dodecanediohydrazide, hexamethylene diamine, stearic acid diethylene amine, xitothane, polyethylene-imine, polyaryl amine, amino-modified acrylic polymers, and the like. These compounds may be used alone or in combination of more than two compound thereof.

In the invention, an impregnation or immersion treatment with the amine compounds can be carried out by means of an aqueous solution or aqueous emulsified dispersion. Use of a water-soluble polyamine is preferred. This is because the treatment bath composed of aqueous solution is stable with the use of water, and because a firm linking bond between the amino group and the acid group as well as a high bond ratio therebetween is successfully attained with the use of a water-soluble amine compound. When use is made of a polyamine compound which is not water-soluble, the bond ratio obtainable is somewhat lowered.

Use of a water-soluble polyamine compound having a molecular weight ranging from 1,000 to 200,000 is especially preferred. When the molecular weight is less than 1,000, the bond ratio per pair of the molecular chain constituting acrylic fiber and the molecular chain constituting a water-soluble polyamine compound becomes low so that the water-soluble polyamine compound becomes detached since breakage of the bond occurs easily during dyeing treatment. Accordingly, the molecular weight less than 1,000 cannot be utilized. A molecular weight exceeding 200,000, is not preferred because hand touch of fiber or texture becomes deteriorated. Further, in such high level of molecular weight, a cohesion of the treated fiber may occur since the water-insoluble compound is fixed on the surface of fiber due to poor migration or poor permeation of the compound. Specifically, use of one or two or more compounds selected from a polyethylene-imine, polyaryl amine, amino-modified acrylic polymer is preferable. However, it is noted that a mixed use of a water-soluble polyamine compound with a metallic compound or a metal ion causes the treated fiber to deteriorate in deodorizing fastness in consequence due to formation of a metal complex which is insoluble in water.

In a deodorizing fiber of the invention, a bond ratio of a polyamine compound to an acid group is preferably from 50 - 100 mol%, especially 60 - 100 mol%. When a bond ratio of acid group is less than 50 mol%, the fiber has a poor deodorizing fastness and is not durable against dyeing treatment.

The bond ratio for acid group can be given based determination of the sum of acid group in a fiber and the determination of amount of remaining acid group (hereinafter called as amount of remaining acid group) which is not bonded to the functional group in a polyamine by the following formula:

$$\text{Bond ratio of acid group (mol\%)} = (\text{sum of amount acid group} - \text{amount remaining acid group}) / \text{sum of acid group} \times 100$$

A deodorizing fiber of the invention can be prepared by a method comprising contacting a fiber having a prescribed amount of an acid group with a water-soluble polyamine to be impregnated, subsequently heat treating the impregnated fiber to bind the amino group in the water-soluble polyamine to 70 - 100% of the acid group such as carboxyl or sulfonic

group so that the residual polyamine group having amino group is fixedly held on the fiber substrate. The heat treatment can be carried out in a dry heat atmosphere at an ambient temperature of 100°C or more. But this method of heat treatment is time consuming, heat treatment by a wet heat condition may be preferred. A wet heat treatment condition used herein, is carried out in a pressurized steam at a temperature of 100°C - 180°C, preferably at a temperature of 105°C - 130°C for from about 30 seconds to 10 minutes. A temperature of the pressurized steam of less than 100°C cannot be used in the invention because a sufficient level of bond between a polyamine compound containing amino group and an acid group in the fiber cannot be promoted consequentially causing the amine compound containing amino group to be readily detached (stripped off) during washing in the final product. A temperature of steam exceeding 180°C cannot be used because a remarkable deterioration of hand touch of the product fiber may result.

The contacting the fiber with a water soluble-amine compound can be carried out by immersing the fiber in an aqueous solution of the water-soluble polyamine compound and subsequently squeezed to remove an excessive liquid. In the treatment, a concentration of the water-soluble polyamine in the aqueous solution ranges from about 0.01-about 20% by weight, although the concentration is varied depending on conditions of immersion and squeezing in a specific operation. The amount of impregnation is adjusted at 0.05 - 10% by weight based on the weight of fiber by means of dehydration using a mangle or centrifuge. Temperature of the aqueous solution at the immersion may be optionally selected. An operational mode of heat treatment may be determined in accordance with the dimensional (shape) form of fiber and carried out using a conventional apparatus available at textile processing plant. In the case where the fiber is a continuous goods, for example, in the form of tow, woven fabric, knitted fabric and nonwoven fabric, the textile goods subsequent to dipping and padding is suitably heat treated by application of a tenter or steamer, tow-reactor, moist heat treating machine with cross-wise spreader. In the case where textile goods is a final textile article such as sweater and the like, the heat treatment can be carried out using a batch-wise drier, a tumble drier, or a wet heat tumbling machine.

It is noted that the fiber subsequent to heat treatment should be washed for removal of an excessive polyamine compound adhered to the fiber.

In the case where the fiber is an acrylic fiber, an especially preferred method for impregnation of a water-soluble polyamine compound to the fiber is carried out by contacting the water-soluble polyamine compound with the fiber in a never-dried state (frequently called as wet-gel fiber) in which a consequent fiber in a suitable stretching subsequent to a wet-spinning of the fiber has never been dried. A never-dried fiber as herein referred to means an acrylic fiber in an aqueous swollen state (undried fiber) before the acrylic fiber structure becomes irreversibly densified by drying and an acrylic fiber having an initial swelling degree (Qc) of 50 - 250% by weight, preferably 60 - 200% by weight; the initial swelling degree is defined below:

$$Qc (\%) = (W_1 - W_2) / W_2 \times 100$$

(In the formula,  $W_1$  represents a weightings (g) of a specimen weighing several grammes of a fiber which has never been dried, centrifuged at 900G at 25°C for 5 minutes, and  $W_2$  represents a weightings of the specimen after drying at 105°C for 2 hours.)

A decrease in residual acid group and a degree of bond for a acid group are attained when a heat treatment at a dried conditions is carried out after a water-soluble polyamine was impregnated to an undried acrylic fiber. Further decrease in the residual acid group and increase in degree of bond of the acid group are attained when a steam treatment is carried out after the heat treatment. This is because an ionic intermolecular cross-linking reaction between the acid group in the cross section of acrylic fiber and the amino group in water soluble polyamine is promoted by the moist heat treatment. Such function of the undried fiber is specific to acrylic fiber and cannot be presented by various cellulosic fibers, polyamide fibers and polyester fibers.

The deodorizing fiber of the invention prepared in accordance with the manner as the above-mentioned is a fiber which exhibits deodorizing effect in virtue of the presence of amino group, and the fiber, as a raw material for making textile goods, can be used singly or in combination with other conventional textile fiber materials to produce end-use textile articles in every shape required through application of every conventional converting method.

Combining with an anionic group-type deodorizing fiber (hereinafter referred to as deodorizing fiber [B]), preferably with a deodorizing fiber which exhibits deodorizing characteristic towards tobacco smoke smell, the deodorizing fiber (hereinafter referred to as deodorizing fiber [A]) of the present invention can make an extensive deodorizing textile product having a deodorizing characteristics towards a broad smell spectrum.

As methods for combining a deodorizing fiber [A] with a deodorizing fiber [B], blend spinning, combination of filament yarn, twisted union yarn, union cloth wearing plaited knitting, or the like can be enumerated. With use of these methods, converted textile goods having a broad deodorizing spectrum in a various forms, for examples, yarns or thread, woven fabric, knitted fabric and nonwoven fabric can be produced for a variety of end-uses.

A fiber composition constituting these textile goods contains, as in combination, at least 5%, preferably at least 10% by weight of deodorizing fiber [A] and at least 0.1%, preferably at least 1% by weight of deodorizing fiber [B]. The composition may contain other conventional fiber as a blending component. Accordingly, with the use of the blend of the fib-

ers as mentioned-above, a textile article in end-use can remove not only smells emitted from carbonyl compounds by virtue of deodorizing fiber [A], but also smells from basic compounds by virtue of deodorizing fiber [B], and can exhibit a durable deodorizing performance towards a compound smell.

A converted textile article can be made of a deodorizing fiber of the present invention and a deodorizing blend of fibers.

An inionic functional group of a deodorizing fiber [B] is carboxyl group or sulfonic group and the content in the fiber is 0.2 - 10 equivalents/kg, preferably 0.4 - 5 equivalents/kg. When a content of carboxyl group is less than 0.2 equivalents/kg, a little deodorizing effect is obtained. A content of carboxyl group exceeding 10 equivalent/kg in the fiber is not preferred because moisture and water absorvencies of the fiber becomes excessively increased and because dimensional (shape) stability and deodorizing fastness of the fiber to washing as well as hand touch of fiber deteriorate.

Carboxyl group and sulfonic group may be contained either singly or concurrently. When an introduction of a greater amount of anionic functional group is required, carboxyl group is preferred since the carboxyl group, which excels sulfonic group in modifying characteristics can be introduced easily. A transition metal can be incorporated with anionic functional group in order to widen kinds of removable smells and in order to enhance deodorizing characteristics.

An anionic functional group, for an example, carboxyl group, can be introduced into fiber by the following methods enlisted by way of examples: a method in which graft polymerization of, for an example, acrylic acid is carried out utilizing for examples, amide group, amino group, and hydroxyl group in the fiber substrate; a method in which, for example, an acrylic fiber is hydrolysed; a method in which a polymer having carboxyl group, for example, acrylic acid is prepared by copolymerizing or by polymer blending. In a further example, the anionic functional group may be introduced by immersing a fiber which is in a never-dried state, obtained immediately after wet spinning into an aqueous solution of the above mentioned polymer, and drying the immersed fiber.

Transition metals as herein referred to includes copper, zinc, iron, nickel, chrome, cobalt and the like, and is introduced into fiber, for example, by immersion technique using a transition metal compounds such as copper compounds ( $\text{CuSO}_4$ ,  $\text{Cu}(\text{NO}_3)_2$  and the like), zinc compounds ( $\text{ZnSO}_4$ ,  $\text{Zn}(\text{NO}_3)_2$  and the like), iron compounds ( $\text{FeSO}_4$ ,  $\text{Fe}(\text{NO}_3)_2$  and the like), nickel compounds ( $\text{NiSO}_4$ ,  $\text{Ni}(\text{NO}_3)_2$  and the like), chromium compounds ( $\text{CrSO}_4$ ,  $\text{Cr}(\text{NO}_3)_2$  and the like), cobalt compounds ( $\text{CoSO}_4$ ,  $\text{Co}(\text{NO}_3)_2$  and the like) and the like. In view of that a remarkable deodorizing is attained, use is made of a copper compound or a zinc compound. A preferred content of a transition metal compound is 0.2 - 10 equivalents/kg fiber, the most preferred is 0.2 - 3 equivalents/kg fiber. When the content is less than 0.2 equivalents/kg fiber, a little deodorizing is obtained. When the content exceeds 10 equivalent/kg fiber, deodorizing effect towards ammonia deteriorates because the content of anionic group becomes a little.

Deodorizing fiber [B] does not decrease in its deodorizing effect even when the fiber is used in blend with cellulosic fiber, acrylic fiber, polyamide fiber, a known deodorizing fiber, or an anti-fungal fiber.

### Examples

The invention will be described in more detail by way of the following Examples. The following Examples, however, are not intended to limit the scope of the invention.

The following are methods of various measurements and evaluations as referred to in the examples.

#### I. Method for evaluation of raw fiber materials

##### (1) Washing Test:

Washing test was carried out in accordance with the method described in JIS-L-0217-Method 103.

##### (2) Measurement of residual acid group:

1g of a sample fiber was immersed in 300 ml of an aqueous solution of sodium chloride having a concentration of 10% by weight and the immersion was shaken in a constant temperature bath at 40°C for 30 minutes. Then, the fiber was, subsequently washed sufficiently with a refined water and dried at 80°C for one hour to prepare a fiber retaining a sodium substituted acid group. The fiber was then treated with in a mixture solution composed of 5 ml of 98% sulfuric acid, 40 ml of 62% nitric acid and 2 ml of 70% perchloric acid on an electricity heater for 5 hours so that wet-decomposition was carried out. The resultant liquid was then diluted by 100 times with a refined water to prepare a dilution for a quantitative estimation of sodium by means of flame spectrum analysis. Quantity of retained acid group was determined using the quantity of the sodium determined by the analysis.

## (3) Evaluation of durability to dyeing of a deodorizing fiber:

A fiber was dyed with Kayanol Milling Blue BW (trade name of an acid dye available from Nippon Kayaku Co. Ltd.; C.I. Acid Blue 138) 3% owf in the presence of Migregal 2N 3% owf as a levelling agent and 0.2 cc/L of 90 weight % aqueous acetic acid solution for pH adjustment at a bath ratio of 1:80 at 100°C for 60 minutes. The dyed fiber was soaped in 1.0 weight % aqueous ammonium solution for 10 minutes to obtain samples for various tests.

## (4) Determination of absorption of an unpleasant smelling substance:

For determination of absorption of an unpleasant smelling substances by a fiber stock, 1.0g of a fiber sample was encapsulated in a Tedlar bag having a volume of 1,000 ml into which a unpleasant smelling substance was introduced together with 600 ml of air cleaned by passing through an active carbon filter and concentration of remaining gas in the Tedlar bag after 60 minutes was determined by using a gas detecting tube to find the quantity of absorbed unpleasant smelling substance. The unpleasant smelling substances used consisted of an aqueous solution containing of 0.04% by weight of acetaldehyde as a representative compound containing carbonyl compound and 10 ml of a gas containing 2,000 ppm of hydrogen sulfide as an acid substance.

## II. Evaluation of a deodorizing textile article made of a blended spun yarn:

## (1) Washing test:

Washing test was carried out in accordance with JIS-L-0217-Method 103.

## (2) Deodorizing characteristics towards a bad-smelling substance

1g of a fiber was encapsulated together with 600 ml of a bad smelling composition in a Tedlar bag and the concentration of the remaining gas was measured using Kitagawa gas detecting tube after 60 minutes. The initial concentrations of the unpleasant smelling components in the unpleasant smelling composition were 100 ppm of acetaldehyde as a carbonyl compound, 40 ppm of acetic acid as an acid compound, 140 ppm of trimethylamine and 140 ppm of ammonia.

## (3) Evaluation of hand touch of a converted textile article:

Evaluation of hand touch for a textile article was performed by a panel consisting of 5 persons. Rating of sensory evaluation was determined by the sum of ratings given by each member of the panel on a sample according to the standard criteria given below:

| Hand touch     | Value of rating |
|----------------|-----------------|
| Not stiff      | 3               |
| Slightly stiff | 2               |
| Stiff          | 1               |

## (4) Evaluation of deodorizing characteristics on a tobacco smoke

Sensory evaluation of deodorizing characteristics on a tobacco smoke was performed by a panel consisting of 16 persons. Rating of evaluation was determined on a sample by the sum of ratings given by each member of the panel according to the standard criteria given hereinafter.

A by-stream of smoke emitted during smoking of a piece of cigarette Mild Seven® (a product of Japan Tobacco Company) was collected for a period of 10 minutes into a Meyer flask having a volume of 2 liters. Using a syringe, 0.5 ml from the collected smoke was introduced into a Mayer flask having a volume of 600 ml. Then, 1g of each sample fiber was introduced into the flask. After the sample fiber had been left standing for two hours, the smell within the flask and the smell of the fiber itself were rated by means of perceptions of each member of the panel according to the standard criteria given below:

| Ratings by human perception: | Ratings |
|------------------------------|---------|
| No effect perceptible        | 1       |
| Almost perceptible           | 2       |
| Slight effect is perceptible | 3       |
| Fair effect is perceptible   | 4       |

[Examples 1 - 8, Comparative Example 1]

94.5% by weight of acrylonitrile, 5.0% by weight of methyl acrylate and 0.5% by weight of sodium metharyl sulpho-  
nate were copolymerized to obtain a copolymer. A spinning dope containing 15.5% by weight of the polymer was pre-  
pared by dissolving the copolymer in 70 weight % nitric acid.

The spinning dope was spun in a nitric acid based coagulating bath containing 37% by weight of nitric acid kept at  
0°C through a spinneret with fine holes having a diameter of 0.06 mm in the form of tow, and the tow was subsequently  
stretched 9 times in a boiling water bath after washing to obtain a undried fiber. The sulfonic acid group content in the  
fiber was found 0.056 mole/kg fiber.

The undried fiber was treated by immersing in aqueous solutions (20°C) of polyethylene-imine (manufactured by  
Nippon Shokubai Company Ltd.) having a degree of polymerization of 1630 (molecular weight about 70,000). The  
immersion was carried out for 1 minute and subsequently was dehydrated at a pick-up of 80% by weight. The concen-  
trations of the polyimine in the immersing solutions were 1.3% by weight (Example 1), 2.5% by weight (Example 2),  
3.8% by weight (Example 3), 6.3% by weight (Example 4) and 12.5% by weight (Example 5). After dehydration, the  
dipped fibers were dried at 80°C for a hour, and were subjected to wet-heat (moist heat) treatment for 5 minutes in a  
saturated steam at 120°C in an autoclave to obtain the fibers of Examples 1 through 5.

For Comparative Example 1, an immersion treatment of the polyethylene-imine aqueous solution was carried out  
in a similar manner in Example 2, in which the polyethylene-imine aqueous solution was brought at pH 4 by an addition  
of phosphoric acid to be substituted by a phosphate of polyethylene-imine having a polymerization degree of 1630  
(molecular weight 70,000) to prepare a comparative fiber. The obtained fibers, fibers after ten times of repeated wash-  
ings and the dyed fibers were tested on absorption of offensive smell substances. The results of the tests and bond  
ratios of acid groups are summarized in Table 1.

[Examples 6, 7]

A fiber (Example 6) was prepared by a modified process according to Example 2 excepting the wet heat treatment.

Replacing the wet heat treatment in Example 2 for treatment by a saturated steam at 190°C for 5 minutes, Example  
2 was repeated to obtain the fiber of Example 7.

The obtained fiber (Example 7) and the fiber after 10 times of repetition of washing and the fiber after dyeing were  
tested on the absorption of offensive smell substances. The results and bind ratios of acid group are tabulated in Table  
1.

[Example 8]

The undried fiber as used in Example 1 was dehydrated and was dried for 1 hour. The dried fiber was then wet heat  
treated in an autoclave with a saturated steam at 120°C for 5 minutes and was subsequently treated by immersing in  
an aqueous solution containing 12.0% by weight of a polyethylene-imine having a molecular weight of 70,000 at a tem-  
perature of 20°C for 1 minute, and finally dehydrated at a pick-up of 17 weight %. The treated fiber was dried at 80°C  
for 1 hour to obtain the fiber of Example 8.

The obtained fiber, the fiber after 10 times of repetition of washing and the fiber after dyeing were tested on the  
absorption of offensive smell substances. The results and bind ratios of the acid group are tabulated in Table 1.

[Table 1]

|             | Amine Compounds                     |                   | Bond ratio of acid group | Deodorizing characteristics of fiber |                  | Deodorizing characteristics of fiber after 10 repetition of washing |                  | Deodorizing characteristics of fiber after dyeing |                  | Adhesive cohesion of fibers |
|-------------|-------------------------------------|-------------------|--------------------------|--------------------------------------|------------------|---|------------------|---|------------------|-----------------------------|
|             | Content of amino group mol/kg fiber | Salt-substitution |                          | Aldehyde                             | Hydrogen sulfide | Aldehyde  | Hydrogen sulfide | Aldehyde  | Hydrogen sulfide |                             |
|             |                                     |                   | mol%                     | mg equivalent/kg fiber               |                  | mg equivalent/kg fiber  |                  | mg equivalent/kg fiber                            |                  |                             |
| Example 1   | 0.06                                | none              | 70                       | 2.0                                  | 0.5              | 1.4   | 0.3              | 1.2   | 0.5              | none                        |
| Example 2   | 0.12                                | none              | 83                       | 3.6                                  | 0.6              | 2.9   | 0.5              | 2.5   | 0.5              | none                        |
| Example 3   | 0.18                                | none              | 92                       | 4.5                                  | 0.7              | 3.3   | 0.5              | 3.0   | 0.5              | none                        |
| Example 4   | 0.30                                | none              | 93                       | 4.5                                  | 0.7              | 3.8   | 0.7              | 3.4   | 0.7              | none                        |
| Example 5   | 0.60                                | none              | 93                       | 4.5                                  | 0.7              | 4.5   | 0.7              | 3.5   | 0.7              | none                        |
| Comparative | 0.18                                | done              | 5                        | 0.5                                  | 0.1              | 0.9   | 0.2              | 0.1   | 0                | none                        |
| Example 1   |                                     |                   |                          |                                      |                  |   |                  |   |                  |                             |
| Example 6   | 0.12                                | none              | 32                       | 3.6                                  | 0.6              | 0.7   | 0.1              | 0.6   | 0.2              | none                        |
| Example 7   | 0.12                                | none              | 92                       | 3.6                                  | 0.6              | 0.2   | 0.1              | 2.1   | 0.4              | observed                    |
| Example 8   | 0.18                                | none              | 5                        | 4.0                                  | 0.7              | 0.7   | 0.2              | 0.7   | 0.1              | none                        |

As clearly shown in Table 1, the fibers according to Examples 1 - 5 exhibit excellent deodorizing characteristics towards acetaldehyde and hydrogen sulfide smells even after the fibers were subjected to 10 times of repeated washing

treatments or to dyeing process. In contrast, the fiber according to Comparative Example 1 has a lower acid group bond ratio in comparison with the fiber according to Examples 2 at the same level of the build up, and the ratio of fall in the deodorizing characteristics towards acetaldehyde and hydrogen sulfide smells of the fiber subjected to ten times of repeated washing (and dyeing process) relative to that of the fiber prior to the washing (and the dyeing process) was greater in comparison with the ratio of fall for the fiber according to Example 2.

The fibers obtained according to Examples 6 and 8 in which the fiber were heat treated after polyethylene-imine treatment. These fibers exhibit, regardless of conditions of heat treatments applied, exceedingly excellent deodorizing fastness to washing (to dyeing processing) than the fiber according to Comparative Example 1 does.

The fiber obtained according to Example 7 in which a treatment with a steam was applied to the fiber had an adherent cohesion between fibers.

#### [Example 9]

The undried fiber as used in Example 1 was immersed in an aqueous dispersion containing 6.3% by weight of a polyethylene-imine (Molecular weight is about 70,000.) and 10% by weight of phthalocyanine copper complex at 20°C for one minute and was subsequently dried at 80°C for 1 hour, and the dried fiber was then treated with a saturated steam at 120°C in an autoclave for 5 minutes to obtain a modified fiber. Absorption test of unpleasant smelling substances was carried out on the fiber as obtained, the obtained fiber after 10 repetition of washing and the obtained fiber as dyed. The results obtained are summarized together with acid group bond ratio in Table 2.

#### [Examples 10 - 12, Comparative Example 2]

A carboxymethyl cellulose fiber containing carboxyl group in a ratio of 1.85 mol/kg fiber was treated by immersing aqueous solutions of xithothane at 20°C for a period of 1 minute; the solutions contain chitosan 0.3% by weight (Comparative Example 2), 5.0% by weight (Example 10), 10.0% by weight (Example 11) and 30% by weight (Example 12) respectively. The immersions were squeezed at a pick up ratio of 100% by weight to obtain the dehydrated fibers. After the dehydrated fibers were then dried at 120°C for 15 minutes, the dried fiber was then treated with a saturated steam at 120°C in an autoclave for 3 minutes to obtain a modified fiber. Absorption tests of unpleasant smelling substances was carried out on the fibers as obtained, the obtained fiber after 10 repetition of washing and the obtained fiber as dyed. The results obtained are summarized together with acid group bond ratios in Table 2.

[Table 2]

|                       | Amine Compound                      |                     | Bond ratio of acid group | Deodorizing characteristics of fiber                    | Deodorizing characteristics of fiber after 10 repetition of washing | Deodorizing characteristics of fiber after dyeing       | Adhesive cohesion of fibers |
|-----------------------|-------------------------------------|---------------------|--------------------------|---|---|---|-----------------------------|
|                       | Content of amino group mol/kg fiber | Solubility in water |                          | Acetaldehyde Hydrogen sulfide<br>mg equivalent/kg fiber | Acetaldehyde Hydrogen sulfide<br>mg equivalent/kg fiber             | Acetaldehyde Hydrogen sulfide<br>mg equivalent/kg fiber |                             |
| Example 4             | 0.30                                | S                   | 93                       | 4.5   | 3.8   | 3.4   | none                        |
| Example 9             | 0.30                                | I                   | 8                        | 0.8   | 0.7   | 0.6   | observed                    |
| Example 10            | 0.31                                | S                   | 51                       | 2.2   | 1.8   | 0.9   | none                        |
| Example 11            | 0.62                                | S                   | 63                       | 2.5   | 2.5   | 1.3   | none                        |
| Example 12            | 1.89                                | S                   | 89                       | 4.5   | 4.5   | 1.8   | none                        |
| Comparative Example 2 | 0.02                                | S                   | 41                       | 0.2   | 0   | 0   | none                        |

\* Water-solubility of amine compound: S, water-soluble; I, water-insoluble

As seen from Table.1, regardless of the kind of amino group contained, the fibers containing amino group at a concentrations of 0.3 - 1.89/kg fiber which were prepared according to Examples 9 - 12, have good deodorizing characteristics towards acetaldehyde and hydrogen sulfide smells over the fiber containing amino group at a concentration of

0.02 mole/kg fiber according to Comparative Example 2, in reference to the fiber as obtained, the fiber subjected to ten times of repeated washing.

#### [Comparative Example 3]

A spinning dope containing 16% by weight of a polymer obtained by copolymerizing 79.0 by weight of acrylonitrile, 21% by weight of acrylic acid was prepared by dissolving the polymer in an aqueous nitric acid of which concentration was 75% by weight. The spinning dope was extruded into a nitric acid-based coagulating bath containing 25% by weight of nitric acid at 0°C through a spinneret having holes with a diameter of 0.06 mm and the coagulated fiber was subsequently stretched 8 times in a boiling water after being washed to obtain an undried fiber. The carboxyl content of the undried fiber was found 2.72 mole/kg fiber.

The undried fiber was immersed in an ethanol solution of a polyethylene-imine having a polymerization degree of 1,680 (molecular weight: 70,000) at a concentration of 2% by weight at 20°C for 3 minutes and was subsequently dehydrated at a pick up ratio of 150% by weight. After the dehydration, the fiber was dried at a temperature of 60°C for 60 minutes to obtain the fiber of Comparative Example 8. Absorption test of unpleasant smelling substances was carried out on the fiber as obtained, the obtained fiber as treated by 10 repetition of washing and the obtained fiber as dyed. The results are tabulated together with acid group bond ratios in Table 4.

The rate of change in weight of fiber after washing test was determined by the following formula:

$$\text{Rate of change in weight of fiber after washing test (\%)} = (W_1 - W_3)/W_1 \times 100$$

in which  $W_1$  represents the weight of dried specimen before the washing test and  $W_2$  represents the weight of the dried specimen after the washing test.

[Table 3]

|                       | Amino group content | Acid group content | Deodorizing characteristics of fiber | Deodorizing characteristics of fiber after 10 repetition of washing | Weight change of fiber after washing | Deodorizing characteristics of fiber after dyeing |
|-----------------------|---------------------|--------------------|--------------------------------------|---|--------------------------------------|---|
|                       | mol/kg              |                    | Acetaldehyde mg equivalent/kg fiber  | Acetaldehyde mg equivalent/kg fiber                                 | (%)                                  | Acetaldehyde mg equivalent/kg fiber               |
| Comparative Example 3 | 0.18                | 0.272              | 4.5                                  | 0.6   | 13.8                                 | 0.0   |
| Example 2             | 0.12                | 0.06               | 3.6                                  | 2.9   | 1.3                                  | 2.5   |

As seen in Table, the fiber of Comparative Example 3 which contained carboxyl group at a ratio of 2.5 mole/kg fiber or more, exhibited an elution under repetition of washing treatment and in consequence the deodorizing characteristic of the fiber towards acetaldehyde became extremely low after 10 repeats of washing or after dyeing treatment.

#### [Examples 13 - 17, Comparative Examples 4 - 3]

A copolymer obtained by copolymerizing 74.7% by weight of acrylonitrile, 25.0% by weight of vinylidene chloride and 0.3% by weight of sodium metharyl sulphonate was dissolved in dimethylformamide to prepare a spinning dope having a polymer concentration at 18% by weight. The spinning dope was, then, extruded through a spinneret with holes having a diameter of 0.15 mm into a dimethylformamide-based coagulating bath containing 75% by weight of dimethylformamide which was kept at 30°C. The obtained fiber was stretched 5 times in a dimethylformamide-based stretching bath containing 75% by weight of dimethylformamide and the stretched fiber was then stretched 1.2 times in a boiling water after washing. The obtained undried had a swelling degree of 95.3% by weight. The content of sulfonic group in the fiber was found 0.10 mole/kg fiber.

The fiber was immersed in aqueous solutions having a pH of 10 of a polyaryl amine having a molecular weight of about 30,000 at various concentrations; 0.03% by weight (Comparative Example 4), 0.15% by weight (Example 13), 0.5% by weight (Example 14), 3.0% by weight (Example 15), 5.0% by weight (Example 16), 10.0% by weight (Example 17) and 15.0% by weight (Comparative Example 5). The immersions were carried out at 25°C for 1 minute and the

immersed fibers were dehydrated at a pick up of 100% by weight. After dehydration, the treated fibers was dried at a temperature of 80°C for 1 hour and were subsequently treated under wet heat using an saturated steam at 120°C to obtain the fibers of Examples 13 - 17 and Comparative Examples 4 - 5.

The obtained fibers, the obtained fiber after 10 times of repeated washings and the obtained fibers as dyed were tested on absorption of unpleasant smell components. Results of the tests and bond ratios of acid group are shown in Table 4.

10

15

20

25

30

35

40

45

50

55

[Table 4]

|                       | Amino group content mol/kg fiber | Solubility of amine | Bond ratio of acid group mol% | Deodorizing characteristics of fiber |                  | Deodorizing characteristics of fiber after 10 repetition of washing | Deodorizing characteristics of fiber after dyeing |                  | Adhesive cohesion of fibers |
|-----------------------|----------------------------------|---------------------|-------------------------------|--------------------------------------|------------------|---|---|------------------|-----------------------------|
|                       |                                  |                     |                               | Acetaldehyde                         | Hydrogen sulfide |   | Acetaldehyde                                      | Hydrogen sulfide |                             |
|                       |                                  |                     |                               | mg equivalent/kg fiber               |                  |   | mg equivalent/kg fiber                            |                  |                             |
| Example 13            | 0.034                            | S                   | 51                            | 1.4                                  | 0.4              | 1.2   | 1.1   | 0.4              | none                        |
| Example 14            | 0.114                            | S                   | 63                            | 1.8                                  | 0.5              | 1.6   | 1.5   | 0.4              | none                        |
| Example 15            | 0.682                            | S                   | 85                            | 3.0                                  | 0.7              | 2.5   | 2.3   | 0.4              | none                        |
| Example 16            | 1.136                            | S                   | 87                            | 4.5                                  | 0.7              | 3.3   | 3.1   | 0.5              | none                        |
| Example 17            | 2.273                            | S                   | 93                            | 4.5                                  | 0.7              | 3.8   | 3.4   | 0.7              | none                        |
| Comparative Example 4 | 0.006                            | S                   | 12                            | 0.7                                  | 0.1              | 0.0   | 0.0   | 0.0              | none                        |
| Comparative Example 5 | 3.409                            | S                   | 93                            | 4.5                                  | 0.7              | 4.1   | 4.0   | 0.7              | observed                    |

\* Solubility of amine: Reference to solubility of amine. S refers to water-soluble, I, insoluble in water respectively.

As clearly shown in Table 4, in comparison with the fiber according to Comparative Example 4 in which the fiber contains the bonded amino group at a concentration of 0.006 mol/kg fiber, the fibers according to Examples 13 - 17 in which the fibers were brought to contain the bonded amino group in quantities of 0.034 - 0.27 mole/kg fiber by using

aqueous solutions at pH 10 of polyaryl amine at pH 10 exhibited excellent deodorizing characteristics of the fiber towards acetaldehyde and hydrogen sulfide smells with reference to the fiber after ten times repetition of washing and the fiber after dyeing. The fibers according to these Examples produce no conglutination of fiber, whereas the fiber according to Comparative Example 1 in which the fiber contained the amino group at a concentration of 3.41 mol/kg fiber produced an intense conglutination.

[Examples 18 - 21]

A polymer prepared by copolymerizing 94.6% by weight of acrylonitrile, 5.0% by weight of methyl acrylate and 0.4% by weight of itaconic acid was dissolved in 70 weight % nitric acid to obtain a spinning dope containing the polymer at a concentration of 16% by weight. The spinning dope was extruded into a nitric acid-based coagulating bath containing nitric acid at a concentration of 35% by weight kept at a temperature of 0°C, and the resultant coagulated fiber after washing was subsequently stretched 8 times in a boiling water to obtain an undried fiber. The undried fiber contained carboxyl group in a quantity of 0.06 mole/kg fiber.

The undried fiber was immersed at 20°C for one minute in aqueous solutions of polyethylene-imine having a molecular weight of 70,000 in which the aqueous solutions contain the polyethylene-imine at a concentration of 1.3% by weight (Example 18), 2.5% by weight (Example 19), 3.8% by weight (Example 20), and the immersions were subsequently dehydrated (pick up was 80% by weight). After the dehydration, the treated fibers were dried at 80°C for 1 hour and were treated by wet heat using a saturated steam at 120°C in an autoclave for 5 minutes to obtain fibers according to Examples 18 - 20. For the fiber according to Example 21, a fiber according to Example 14 except that wet heat was eliminated, was allocated.

The obtained fibers, the obtained fiber after 10 times of repeated washings and the obtained fibers as dyed were tested on absorption of unpleasant smell substances. Results of the tests and bond ratios of acid group are shown in Table 5.

(Table 5)

|            | Steam treatment | Bond ratio of acid group<br>mol% | Deodorizing characteristics of fiber | Deodorizing characteristics of fiber after 10 repetition of washing |  | Deodorizing characteristics of fiber after dyeing |  |
|------------|-----------------|----------------------------------|--------------------------------------|---|--|---|--|
|            |                 |                                  |                                      | Acetaldehyde<br>mg equivalent/kg fiber                              | Hydrogen sulfide<br>mg equivalent/kg fiber | Acetaldehyde<br>mg equivalent/kg fiber            | Hydrogen sulfide<br>mg equivalent/kg fiber |
| Example 18 | done            | 70                               | 2.0                                  | 1.2   | 0.5  | 1.8   | 0.4  |
| Example 19 | done            | 81                               | 3.5                                  | 2.5   | 0.5  | 1.8   | 0.4  |
| Example 20 | done            | 89                               | 4.5                                  | 3.0   | 0.5  | 2.6   | 0.4  |
| Example 21 | none            | 45                               | 3.6                                  | 0.8   | 0.2  | 0.8   | 0.2  |

As shown in Table 5, the fibers according to Example 1 - 20 exhibits excellent deodorizing characteristics towards acetaldehyde odor and hydrogen sulfide odor regarding the fibers after 10 times of repeated washing test and the dyed fiber, in comparison with the fiber according to Example 21 in which the steam treatment was omitted.

[Examples 22 - 25]

The never dried fiber used in Example 1 which was prepared by stretching 9 times in boiling water, was immersed at 20°C for 1 minute in aqueous solutions of polyethylene-imines differing in molecular weight at a concentration of 1% by weight; the molecular weights of polyethylene-imine are about 300 (Example 22), about 1,2000 (Example 23), about 10,000 (Example 24) and about 70,000 (Example 25). The immersed fibers were dehydrated by squeezing at a pick up ratio of 100%. The dehydrated fibers were dried at 120°C for 15 minutes and subsequently wet-heat treated by a saturated steam at 120°C in an autoclave to obtain fibers according to Examples 22 - 25.

The fiber as obtained, the fibers after ten times of repeated washing test and the dyed fiber of the obtained fiber were tested on the offensive smell absorption test. The results obtained and bond ratios of acid groups are tabulated in Table 6.

[Table 6]

|            | Polyethylene-<br>imine<br>molecular<br>weight | Bond ratio<br>of acid<br>group<br><br>mol% | Deodorizing<br>characteristics<br>of fiber |   | Deodorizing<br>characteristics<br>of fiber<br>after 10 repetition<br>of washing |   | Deodorizing<br>characteristics<br>of fiber<br>after dyeing |   |
|------------|---|--|--|---|---|---|--|---|
|            |   |  | Acetaldehyde<br>mg equivalent/kg fiber     | Hydrogen<br>sulfide<br>mg equivalent/kg fiber | Acetaldehyde<br>mg equivalent/kg fiber  | Hydrogen<br>sulfide<br>mg equivalent/kg fiber | Acetaldehyde<br>mg equivalent/kg fiber                     | Hydrogen<br>sulfide<br>mg equivalent/kg fiber |
| Example 22 | 300   | 35   | 1.4  | 0.3   | 1.0   | 0.3   | 0.6  | 0.1   |
| Example 23 | 1,200   | 53   | 1.5  | 0.4   | 1.1   | 0.3   | 1.0  | 0.3   |
| Example 24 | 10,000  | 68   | 2.0  | 0.5   | 1.3   | 0.3   | 1.2  | 0.5   |
| Example 25 | 70,000  | 70   | 2.0  | 0.5   | 1.4   | 0.5   | 1.2  | 0.5   |

As shown in Table 6, the fibers according to Examples 24 - 27 which contain bonded polyethylene-imines having a molecular weight of 300 - 70,000 exhibit excellent deodorizing characteristics towards acetaldehyde and hydrogen sulfide smells even after they had been subjected to 10 times of washing test. In comparison with the fiber according to

Example 22 which contains a bonded polyethylene-imine having a molecular weight of 300, the fibers according to Examples 23 - 25 which contain bonded polyethylene-imines having a molecular weight of 12,000 - 70,000 exhibit little deterioration in deodorizing characteristics towards acetaldehyde and hydrogen sulfide smells even after they were dyed.

[Example 26]

A woven fabric (weave density: 35 ends/inch, 35 picks/inch) were made from a spun yarn of 10 Nm composed of a blend fibers in which the fiber according to Example 2, Cashmilon FK (a conventional acrylic fiber available from ASAHI KASEI KOGYO KABUSHIKI KAISYA) and a fiber obtained by spinning a copolymer by copolymerizing acrylonitrile and acrylic acid in a ratio of 80 to 20 by weight in a 75% nitric acid spinning bath were blended in a mixing ratio of 3:1:6.

[Example 27]

A woven fabric was made of a blended spun yarn which was prepared by mixing a fiber according to Example 2, a transition metal-containing fiber and Cashmilon FK (an acrylic fiber available from ASAHI KASEI KOGYO KABUSHIKI KAISYA) at a mixing ratio of 3:1:6 according to the Example.

The transition metal-containing fiber was prepared by spinning a polymer obtained by copolymerizing acrylonitrile and acrylic acid in a ratio of 80 to 20 by weight into a 75% nitric acid bath, and was immersed in an aqueous solution of sodium hydroxide at a concentration of 20% by weight containing 1.5 mol/liter of sodium chloride at 20°C, and was subsequently dipped in an aqueous solution containing 10% by weight of cupric sulfate, and followed by drying after washing and dehydration.

[Comparative Example 6]

A woven fabric made of an acrylic fiber containing 0.06 mole of sulfonic acid was treated by immersing in an aqueous solution containing 12% by weight of an polyethylene-imine having a molecular weight of 70,000 at 20°C for 1 minute and was subsequently dehydrated at a pick-up ratio of 17% by weight. The treated fabric was, then, dried at 80°C for 1 hour to obtain a fiber according to Comparative Example 6.

The woven fabrics of Examples 29, 27 and Comparative Example 6 were evaluated on their characteristics towards various kinds of unpleasant smells in contrast to those of the fabrics after ten times of repeated washing. The results of evaluations are shown in Table 7.

In reference to Table 7, the fibers according to Examples 26 and 28 exhibit good characteristics with the fibers after ten times of repeated washing in comparison with those of the fiber according to Comparative Example 6. In addition, the fiber according to Examples 28 and 29 had good hand touch as shown in Table 7.

[Table 7] Residual gas concentration (ppm) in deodorizing test

|                       | Ratings of deodorizing characteristics of fiber |              |             |                  |         |                 | Hand touch rating | Tobacco smoke sensory test (Over all ratings) |
|-----------------------|---|--------------|-------------|------------------|---------|-----------------|-------------------|---|
|                       | Offensive smells                                | Acetaldehyde | Acetic acid | Hydrogen sulfide | Ammonia | Trimethyl amine |                   |   |
|                       | Initial concentration of offensive smell (ppm)  | 100          | 40          | 25               | 140     | 140             |                   |   |
| Example 26            | no washing                                      | 22           | 0           | 0                | 0       | 0               | 15                | 74  |
|                       | after 10 repetition of washing                  | 26           | 0           | 0                | 0       | 0               | 15                | 76  |
|                       | no washing                                      | 25           | 0           | 0                | 1       | 5               | 15                | 71  |
| Example 27            | after 10 repetition of washing                  | 27           | 0           | 0                | 0       | 3               | 15                | 73  |
|                       | no washing                                      | 25           | 0           | 0                | 138     | 135             | 5                 | 43  |
| Comparative Example 6 | after 10 repetition of washing                  | 88           | 35          | 23               | 129     | 131             | 10                | 25  |

[Examples 28 - 31, Comparative Example 7 - 8]

Woven fabrics were made of spun yarns obtained by blending the fiber obtained in Example 2, fibers prepared by immersing the never-dried fibers gathered midway during the preparation of the fiber in Example 2 into aqueous solution of polyacrylic acid so as to contain carboxyl group at varying contents of from 0.1 mole to 15.0 mole/kg fiber and Cashimilon FK (an acrylic fiber available from ASAHI KASEI KOGYOU KABUSHIKI KAISYA), in an mixing ratio of 3:0.5:6.5.

The respective contents of carboxyl group contained in the respective fibers for the respective woven fabrics are tabulated along with characteristics of the liners towards unpleasant smells are tabulated in Table 8.

[Table 8] Residual gas concentration (ppm) in deodorizing test

|                       | Offensive smell                                |  | Acetaldehyde | Acetic acid | Hydrogen sulfide | Ammonia | Trimethyl amine | Hand touch ratings | Tobacco smoke sensory test (overall ratings) |
|-----------------------|--|--|--------------|-------------|------------------|---------|-----------------|--------------------|--|
|                       | Initial concentration of offensive smell (ppm) | Carb-oxyl group content (mol/kg fiber) |              |             |                  |         |                 |                    |  |
| Comparative Example 7 | 0.1  | washing                                | 23           | 0           | 0                | 15      | 36              | 15                 | 37   |
|                       |  | 10 times                               | 28           | 0           | 1                | 17      | 40              | 15                 | 41   |
| Example 28            | 0.2  | none                                   | 21           | 0           | 0                | 3       | 12              | 15                 | 60   |
|                       |  | 10 times                               | 26           | 1           | 0                | 4       | 16              | 15                 | 62   |
| Example 29            | 0.4  | none                                   | 22           | 0           | 0                | 0       | 0               | 15                 | 77   |
|                       |  | 10 times                               | 23           | 0           | 0                | 0       | 0               | 15                 | 76   |
| Example 30            | 5.0  | none                                   | 20           | 0           | 0                | 0       | 0               | 15                 | 75   |
|                       |  | 10 times                               | 25           | 0           | 0                | 0       | 0               | 15                 | 78   |
| Example 31            | 10.0   | none                                   | 21           | 0           | 0                | 0       | 0               | 15                 | 74   |
|                       |  | 10 times                               | 24           | 0           | 0                | 5       | 10              | 13                 | 63   |
| Comparative Example 8 | 15.0   | none                                   | 20           | 0           | 0                | 0       | 0               | 15                 | 77   |
|                       |  | 10 times                               | 22           | 0           | 0                | 16      | 32              | 5                  | 55   |

Referring to Table 8, it is shown that the woven fabrics (Examples 28 - 31) made of fibers having a content of carb-oxyl group from 0.2 - 10 mole/kg fiber exhibit excellent deodorizing characteristics towards tobacco smells. In addition, these fibers exhibit good deodorizing fastness to washing and the fabric had good handling touch after washing.

[Examples 32 - 35, Comparative Examples 9 - 10]

A spinning dope containing a polymer 18% by weight was prepared by dissolving the polymer in dimethylformamide which was obtained by copolymerizing 74.7% by weight of acrylonitrile, 25.0% by weight of vinylidene chloride and sodium metharyl sulfonate. The spinning dope was extruded through a spinneret having holes having a diameter of 0.15 mm into a coagulating bath containing 75% by weight of dimethylformamide at 30°C, and was subsequently stretched 5 times in a stretching bath containing 75% by weight of dimethylformamide at 80°C and then stretched 1.2 times in a boiling water after being washed.

A fiber prepared from the never-dried fiber as obtained above by a method in which the never-dried fiber was immersed in an aqueous solution containing 3.8% by weight of a polyethylene-imine having a molecular weight of about 70,000 at 20°C for a period of 1 minute, dried at 80°C for 1 hour after dehydration at a pick-up ratio of 80% by weight and subsequently heat-treated by a saturated steam at 120°C in an autoclave for 5 minutes; acrylic fibers containing copper with its content varied ranging from 0.05 - 6 equivalent/kg fiber which is bonded to carboxyl group in an acrylic fiber prepared from a blend of a polymer obtained by copolymerizing acrylonitrile and acrylic acid in a copolymerizing ratio by weight of 80:20 and an polyacrylonitrile in a blending ratio of 30:70, and; a conventional polyester fiber were mixed in a blending ratio of 3:0.5:6.5 for making blended spun yarns to produce woven fabrics.

Deodorizing characteristic towards offensive smells for the woven fabrics were evaluated according to the manner similar to that in Example 20. Contents of copper and results of evaluation on characteristics towards offensive smells are summarized for the respective woven fabrics in Table 9.

[Table 9] Residual gas concentration in deodorizing test

|                        | Offensive smell                      |  | Acetaldehyde | Acetic acid | Hydrogen sulfide | Ammonia | Trimethyl amine | Hand touch ratings | Tobacco smoke sensory test (overall ratings) |
|------------------------|--------------------------------------|--|--------------|-------------|------------------|---------|-----------------|--------------------|--|
|                        | Initial concentration                | concentration of offensive smell (ppm) |              |             |                  |         |                 |                    |  |
|                        | Copper content (equivalent/kg fiber) |  |              |             |                  |         |                 |                    |  |
| Comparative Example 9  | 0.05                                 |  | 23           | 0           | 1                | 13      | 29              | 15                 | 43   |
| Example 32             | 0.1                                  |  | 25           | 0           | 0                | 3       | 9               | 15                 | 63   |
| Example 33             | 0.2                                  |  | 25           | 0           | 0                | 0       | 0               | 15                 | 73   |
| Example 34             | 3.0                                  |  | 22           | 0           | 0                | 0       | 0               | 15                 | 77   |
| Example 35             | 5.0                                  |  | 20           | 0           | 1                | 5       | 4               | 15                 | 64   |
| Comparative Example 10 | 6.0                                  |  | 21           | 0           | 0                | 10      | 44              | 15                 | 57   |

In Table 9, it is shown that woven fabrics (Examples 32 - 35) made of fibers having a copper content of 0.1 - 5 equivalent/kg fiber exhibit not only deodorizing characteristics towards a carbonyl group containing compound, but also deodorizing characteristics towards a tobacco smoke smell, and that they have good hand touch.

[Examples 36 - 40, Comparative Examples 11 - 14]

94.5% by weight of acrylonitrile, 5.0% by weight of methyl acrylate and 0.5% by weight of metharyl sulfonate were copolymerized to prepare a polymer. A spinning dope containing 15.5% by weight of the polymer was prepared by dissolving the polymer in 70% by weight aqueous nitric acid.

A never-dried fiber was prepared by spinning the spinning dope through spinneret with holes having a diameter of 0.6 mm into a nitric acid-based aqueous coagulating bath containing 75.0% by weight of nitric acid kept at a temperature of 0°C and stretch the coagulated fiber 9 times in a boiling water after washing. The never-dried fiber was immersed in an aqueous solution of a polyaryl imine having a molecular weight of about 30,000 at 25°C for 1 minute, then dried at 80°C for about 1 hour after dehydrating at a pick-up ratio of 100% by weight, and was subsequently heat treated by a saturated steam at 120°C for 5 minutes in an autoclave.

The obtained fiber, an acrylic acid-grafted nylon fiber in which acrylic acid was grafted so that carboxyl group is contained in a content of 0.8 mole/kg fiber, and a conventional acrylic fiber (Cashimilon FK available from ASAHI KASEI KOGYO KABUSHIKI KAISHA) were blended in varied blending ratios to make blended spun yarns and knitted fabrics were prepared from the blended spun yarns.

The knitted fabrics were evaluated on their deodorizing characteristics towards offensive smells in accordance with the manners similar to those in Example 20.

In Table 10, the blending ratios of the acrylic fiber containing polyaryl amine and the nylon containing carboxyl group and results of evaluation on deodorizing characteristics towards offensive smells are tabulated for the respective knitted fabrics.

[Table 10] Residual gas concentration (ppm) in deodorizing test

|                           | Blending ratio of fiber<br>(% by weight)            |   |                                  | Initial concentration of offensive smell<br>(ppm) |                |                     |         |                    | Tobacco<br>smoke<br>sensory<br>test<br>(overall<br>ratings) |
|---------------------------|---|---|----------------------------------|---|----------------|---------------------|---------|--------------------|---|
|                           | Polyaryl<br>amine<br>containing<br>acrylic<br>fiber | Carboxyl<br>group<br>containing<br>nylon<br>fiber | Conventional<br>acrylic<br>fiber | Acetaldehyde                                      | Acetic<br>acid | Hydrogen<br>sulfide | Ammonia | Trimethyl<br>amine |   |
|                           |   |   |                                  |   |                |                     |         |                    |   |
| Comparative<br>Example 11 | 0   | 100   | 0                                | 89  | 36             | 24                  | 0       | 0                  | 45  |
| Comparative<br>Example 12 | 1   | 99  | 0                                | 75  | 33             | 23                  | 0       | 0                  | 49  |
| Example 36                | 5   | 95  | 0                                | 40  | 26             | 19                  | 0       | 0                  | 64  |
| Example 37                | 10  | 90  | 0                                | 32  | 14             | 6                   | 0       | 0                  | 71  |
| Example 38                | 30  | 5   | 65                               | 22  | 0              | 0                   | 0       | 0                  | 77  |
| Example 39                | 99  | 1   | 0                                | 21  | 0              | 0                   | 0       | 0                  | 76  |
| Example 40                | 99.9  | 0.1   | 0                                | 20  | 0              | 0                   | 0       | 1                  | 73  |
| Comparative<br>Example 13 | 99.95   | 0.05  | 0                                | 20  | 0              | 0                   | 18      | 42                 | 56  |
| Comparative<br>Example 14 | 100   | 0   | 0                                | 19  | 0              | 0                   | 129     | 136                | 47  |

In Table 10, there are shown that woven fabrics (Examples 36 - 40) composed of the acrylic fibers containing the polyaryl imine in a blending ratio of 5% or more by weight and the carboxyl group-containing nylon in a blending ratio of 0.1 or more by weight deodorize not only smell of carbonyl group-containing but also Smell of acid compounds and

exhibit excellent deodorizing characteristics towards smell of tobacco smoke.

[Examples 41 - 45, Comparative Examples 15 - 18]

5 A polymer obtained by copolymerizing 74.7% by weight of acrylonitrile, 25% by weight of vinylidene chloride and 0.3% by weight of sodium metharyl sulfonate was dissolved in dimethylformamide to obtain a spinning dope containing 18% by weight of the polymer. The spinning dope was spun through a spinneret with holes having a size of 0.15 mm into a coagulating bath maintained at 30°C having a concentration of 75% by weight of dimethylformamide, and was then stretched 5.0 times in a stretching bath containing 75% by weight of dimethylformamide at 80°C bath, and was subsequently stretched in a boiling water after washing.

10 The fiber was treated at 25°C for 1 minute by immersing the fiber in an aqueous solution at pH 10 containing 5.0% containing 5.0% by weight of a polyaryl amine having a molecular weight of about 30,000. The immersed fiber was dehydrated at a pick-up of 100% by weight and dried at 80°C for 1 hour. The dried fiber was subsequently heat treated by a saturated steam in an autoclave at 120°C for 5 minutes.

15 The fiber obtained, an acrylic fiber containing zinc at a content of 0.2 equivalent/kg fiber which was bonded to the carboxyl group introduced by grafting acrylic acid to a conventional acrylic fiber (Cashimilon FK, available from ASAHI KASEI KOGYU KABUSHIKI KAISHA) so that carboxyl group was contained at a content of 2.0 equivalent/kg fiber, and the above-mentioned acrylic fiber (Cashimilon FK) are made into spun yarns composed of the fibers in a blending ratio of 3:0.5:6.5 to obtain woven fabrics therefrom.

20 The woven fabrics were evaluated on their deodorizing characteristics towards offensive smells in accordance with the manners described in Example 20.

In Table 11, the blending ratios of the acrylic fiber containing polyaryl amine and zinc-containing acrylic fiber and results of evaluation on deodorizing characteristics towards offensive smells are tabulated for the respective woven fabrics.

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[Table 11] Residual gas concentration (ppm) in deodorizing test

|                           | Blending ratio of fiber<br>(% by weight)             |   |                                  | Initial concentration (ppm) of offensive<br>smell |                |                     |         |                    | Tobacco<br>smoke<br>sensory<br>test<br>(overall<br>ratings) |  |    |
|---------------------------|--|---|----------------------------------|---|----------------|---------------------|---------|--------------------|---|--|----|
|                           | Polyaryl<br>amine-<br>containing<br>acrylic<br>fiber | Zinc-<br>containing<br>acrylic<br>fiber | Conventional<br>acrylic<br>fiber | Acetaldehyde                                      | Acetic<br>acid | Hydrogen<br>sulfide | Ammonia | Trimethyl<br>amine |   |  |    |
|                           |  |   |                                  |   |                |                     |         |                    |   |  |    |
| Comparative<br>Example 15 | 0  | 100                                     | 0                                | 86  | 33             | 22                  | 0       | 0                  |   |  | 42 |
| Comparative<br>Example 16 | 1  | 99                                      | 0                                | 78  | 31             | 21                  | 0       | 0                  |   |  | 46 |
| Example 41                | 5  | 95                                      | 0                                | 43  | 22             | 17                  | 0       | 0                  |   |  | 66 |
| Example 42                | 10   | 90                                      | 0                                | 30  | 16             | 3                   | 1       | 0                  |   |  | 73 |
| Example 43                | 30   | 5                                       | 65                               | 20  | 0              | 0                   | 1       | 2                  |   |  | 78 |
| Example 44                | 99   | 1                                       | 0                                | 20  | 0              | 0                   | 1       | 1                  |   |  | 75 |
| Example 45                | 99.9   | 0.1                                     | 0                                | 20  | 0              | 0                   | 2       | 3                  |   |  | 72 |
| Comparative<br>Example 17 | 99.95  | 0.05                                    | 0                                | 20  | 0              | 0                   | 18      | 34                 |   |  | 55 |
| Comparative<br>Example 18 | 100  | 0                                       | 0                                | 18  | 0              | 0                   | 135     | 129                |   |  | 47 |

Referring to Table 11, it is shown that woven fabrics (Examples 36 - 40) using the acrylic fibers containing the polyaryl amine in a blending ratio of 5% or more by weight and zinc-containing acrylic fiber in a blending ratio of 0.1 or more by weight deodorize not only smell of carbonyl group-containing but also smell of acid compounds and exhibit

excellent deodorizing characteristics towards smell of tobacco smoke.

[Example 46, Comparative Example 19]

5 A polymer obtained by copolymerizing 94.6% by weight of acrylonitrile, 5% by weight of methyl acrylate and 0.4% by weight of itaconic acid was dissolved in an aqueous nitric acid at a concentration of 70% by weight to obtain a spinning dope containing 16% by weight of the polymer. The spinning dope was spun through a spinneret with holes having a size of 0.06 mm into a nitric acid-based coagulation bath containing 35% by weight of nitric acid of which the bath temperature was maintained at 0°C, and was subsequently stretched 8 times in a boiling water after washing, and  
10 finally dried to obtain a at 80°C bath and subsequently stretched in a boiling water after washing to obtain a never-dried fiber.

The fiber was immersed in an aqueous solution containing a polyethylene-imine having a molecular weight of about 70,000 at a concentration of 2.5% by weight at 20°C for 1 minute, and dried at 80°C for 1 hour after dehydration at a pickup ratio of 80% by weight, and subsequently heat treated by wet heating by a saturated steam at 120°C for a period  
15 of 5 minutes in an autoclave to obtain a treated fiber.

A woven fabric (Example 46) was prepared using a blended spun yarn prepared by blending the above-mentioned fiber, a fiber which was prepared from a blended polymer composition by blending a polymer obtained by copolymerizing acrylonitrile and acrylic acid at a mixing ratio of 80:200 and polyacrylonitrile at a blending ratio of 80:70, and a conventional acrylic fiber at a blending ratio of 3:1:6.

20 Another woven fabric was prepared for Comparative Example 19 in which the fabric was obtained according to the same manner and conditions as those in Example 46 except that the heat treatment by wet heat was omitted.

For the Example and Comparative Example, evaluations of deodorizing characteristic toward offensive smells according to the method described in Example 2 were carried out on the woven fabrics prepared, the woven fabric subsequent to ten times of repeated washing tests and the woven fabric subsequent to dyeing.

25 The results of the evaluations are tabulated in Table 12.

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[Table 12] Residual gas concentration (ppm) in deodorizing test

|                        | Bond ratio of acid group mol% | Ratings of deodorizing characteristics |              |             |                  |         |                 | Tobacco smoke sensory test (overall ratings) |
|------------------------|-------------------------------|--|--------------|-------------|------------------|---------|-----------------|--|
|                        |                               | Offensive smell                        | Acetaldehyde | Acetic acid | Hydrogen sulfide | Ammonia | Trimethyl amine |  |
|                        |                               | Initial concentration (ppm)            |              |             |                  |         |                 |  |
| Example 46             | 81                            | No washing                             | 22           | 0           | 0                | 0       | 0               | 74   |
|                        |                               | Washing 10 times                       | 26           | 0           | 0                | 0       | 0               | 76   |
|                        |                               | After dyeing                           | 32           | 1           | 0                | 1       | 0               | 72   |
| Comparative Example 19 | 45                            | No washing                             | 25           | 0           | 0                | 1       | 0               | 73   |
|                        |                               | Washing 10 times                       | 76           | 35          | 1                | 0       | 0               | 55   |
|                        |                               | After dyeing                           | 69           | 38          | 0                | 1       | 0               | 48   |

In Table 12, it is apparent that an acrylic fiber in which a bond ratio of acid group to polyethylene-imine was made 50 mol/kg fiber or more by applying wet heat treatment in the treatment step of the undried acrylic fiber with a polyethylene-imine, exhibits good deodorizing characteristics towards smells of carbonyl group-containing compounds and

acid compounds on the fiber after 10 times of repetition of washing and the fiber after dyeing.

### Industrial Applicability

The deodorizing fiber according to the invention have a deodorizing characteristics capable of removing offensive smells originating from acid compounds such as carbonyl compounds by adsorption. The deodorizing characteristics of fiber do not deteriorate during textile processing such as dyeing or the like after a number of repeated washing. As a raw material fiber for woven and knitted fabric, the deodorizing fiber of the invention can provide a variety of textile articles covering clothing and interior and furnishings with fast deodorizing characteristics.

Textile converted articles made from a mixture of the deodorizing fiber of the invention with a deodorizing fiber having an anionic functional group in the fiber substrate which is capable of removing offensive smells emitted from a basic compound, can remove a compound smell in which a basic and an acid compounds are involved, and the deodorizing characteristics of the articles are durable.

With the use of a fiber of the invention as a component of a blend, a textile article can exhibit a fast deodorizing effect on a compound smell, for an example, tobacco smoke smell in which various smells are involved.

### **Claims**

1. A deodorizing fiber characterized in that the fiber contains an acid group in the fiber substrate at a proportionate amount of 0.01 - 2.5 mol/kg fiber and an amino group containing compound at a proportionate amount of 0.03 - 3 mol/kg fiber of which at least part of the amino group is carried on the fiber by chemical bonding to the acid group.
2. A deodorizing fiber according to claim 1, characterized in that a proportion of the chemical bonding of the acid group is 50 - 100 mol%.
3. A deodorizing fiber according to claim 1, characterized in that the acid group is carboxyl group or sulfonic group.
4. A deodorizing fiber according to claim 1, characterized in that the compound is a polyamine having a molecular weight of 1,000 - 200,000.
5. A deodorizing fiber according to claim 1, characterized in that the fiber is an acrylic fiber.
6. A process for producing a deodorizing fiber characterized in that a fiber containing an acid group in a proportionate amount of 0.01 - 2.5 mol/kg fiber is impregnated with a solution of a water-soluble polyamine compound having a molecular weight of 1,000 - 200,000 so that the fiber contains the polyamine compound in a proportionate amount of 0.03 - 3 mol/kg fiber in terms of the amino group thereof, and that the impregnated fiber is subsequently heat treated to fix the polyamine compound to the fiber by bonding chemically to the acid group.
7. A process for producing a deodorizing fiber according to claim 6, characterized in that the acid group is carboxyl group or sulfonic group.
8. A process for producing a deodorizing fiber according to claim 6 or 7, characterized in that the fiber is an acrylic fiber.
9. A process for producing a deodorizing fiber characterized in that an acrylic fiber containing an acid group in the fiber substrate at a proportionate amount of 0.01 - 2.5 mol/kg fiber which is yet in a never dried state and subsequent to stretching after to wet spinning, is contacted with a solution of a water-soluble polyamine compound having a molecular weight of 1,000 - 200,000 so that the fiber contains the water-soluble polyamine in a proportionate amount of 0.03 - 3 mol/kg fiber in terms of the amino group thereof, and that the impregnated fiber is subsequently heat treated to fix the polyamine compound to the fiber by binding chemically to the acid group.
10. A process for producing a deodorizing fiber according to claim 9, characterized in that the acid group is carboxyl group or sulfonic group.
11. A textile article having deodorizing characteristics comprising a deodorizing at least 5% by weight of a deodorizing fiber (A) containing an acid group in the fiber substrate at a proportionate amount of 0.01 - 2.5 mol/kg fiber and an amino group containing compound at a proportionate amount of 0.03 - 3 mol/kg fiber of which at least part of the amino group is carried on the fiber by chemical bonding to the acid group and at least 0.1% by weight of a deodor-

izing fiber (B) containing either an anionic functional group in the fiber substrate thereof in a proportionate amount of 0.2 - 10 equivalent/kg fiber, or a transition metal bonded anionic functional group in an proportionate amount of 0.2 - 10 equivalent/kg fiber as blended components.

- 5    12. A textile article having a deodorizing characteristics according to claim 11, the amino group containing compound is a polyamine having a molecular weight of 1,000 - 200,000.
13. A textile article having a deodorizing characteristics according to claim 11 or 12, the transition metal is copper or zinc.
- 10    14. A textile article having a deodorizing characteristics according to any one of claim 11, 12 and 13, the deodorizing fiber is an acrylic fiber.

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## INTERNATIONAL SEARCH REPORT

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PCT/JP96/00651

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl<sup>6</sup> D06M15/61

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl<sup>6</sup> D06M15/61

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                | Relevant to claim No. |
|-----------|---|-----------------------|
| E         | JP, 8-74177, A (Asahi Chemical Industry Co., Ltd.),<br>March 19, 1996 (19. 03. 96) (Family: none) | 1 - 10                |

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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CLAIMS

1. A deodorizing fiber characterized in that the fiber contains an acid group in the fiber substrate at a proportionate amount of 0.01 - 2.5 mol/kg fiber and an amino group containing compound at a proportionate amount of 0.03 - 3 mol/kg fiber of which at least part of the amino group is carried on the fiber by chemical bonding to the acid group.

2. A deodorizing fiber according to claim 1, characterized in that a proportion of the chemical bonding of the acid group is 50 - 100 mol%.

3. A deodorizing fiber according to claim 1, characterized in that the acid group is carboxyl group or sulfonic group.

4. A deodorizing fiber according to claim 1, characterized in that the compound is a polyamine having a molecular weight of 1,000 - 200,000.

5. A deodorizing fiber according to claim 1, characterized in that the fiber is an acrylic fiber.

6. A process for producing a deodorizing fiber characterized in that a fiber containing an acid group in a proportionate amount of 0.01 - 2.5 mol/kg fiber is impregnated with a solution of a water-soluble polyamine compound having a molecular weight of 1,000 - 200,000 so that the fiber contains the polyamine compound in a proportionate amount of 0.03 - 3 mol/kg fiber in terms of the amino group thereof, and that the impregnated fiber is subsequently heat treated to fix the polyamine compound to the fiber by bonding chemically to the acid group.

7. A process for producing a deodorizing fiber according to claim 6, characterized in that the acid group is carboxyl group or sulfonic group.

8. A process for producing a deodorizing fiber according to claim 6 or 7, characterized in that the fiber is an acrylic fiber.

9. A process for producing a deodorizing fiber

characterized in that an acrylic fiber containing an acid group in the fiber substrate at a proportionate amount of 0.01 - 2.5 mol/kg fiber which is yet in a never dried state and subsequent to stretching after to wet spinning, is contacted with a solution of a water-soluble polyamine compound having a molecular weight of 1,000 - 200,000 so that the fiber contains the water-soluble polyamine in a proportionate amount of 0.03 - 3 mol/kg fiber in terms of the amino group thereof, and that the impregnated fiber is subsequently heat treated to fix the polyamine compound to the fiber by binding chemically to the acid group.

10. A process for producing a deodorizing fiber according to claim 9, characterized in that the acid group is carboxyl group or sulfonic group.

(11) A textile article having deodorizing characteristics comprising a deodorizing at least 5% by weight of a deodorizing fiber. (A) containing an acid group in the fiber substrate at a proportionate amount of 0.01 - 2.5 mol/kg fiber and an amino group containing compound at a proportionate amount of 0.03 - 3 mol/kg fiber of which at least part of the amino group is carried on the fiber by chemical bonding to the acid group and at least 0.1% by weight of a deodorizing fiber. (B) containing either an anionic functional group in the fiber substrate thereof in a proportionate amount of 0.2 - 10 equivalent/kg fiber, or a transition metal bonded anionic functional group in an proportionate amount of 0.2 - 10 equivalent/kg fiber as blended components.

12. A textile article having a deodorizing characteristics according to claim 11, the amino group containing compound is a polyamine having a molecular weight of 1,000 - 200,000.

13. A textile article having a deodorizing characteristics according to claim 11 or 12, the transition metal is copper or zinc.

14. A textile article having a deodorizing characteristics according to any one of claim 11, 12 and 13, the deodorizing fiber is an acrylic fiber.

ABSTRACT

Described is a deodorizing fiber having an acid group in the fiber substrate of the fiber in a proportionate amount of 0.01 - 2.5 mol/kg fiber and an amino group containing compound in a proportionate amount of 0.03 - 3 mol/kg fiber and the amino group containing compound being chemically bonded in the fiber between the acid group and at least a part of the amino group contained in the amino group containing compound.

The acid group can be carboxyl group and/or sulfonic acid group. A preferred amino group containing compound is a water soluble polyimine having a molecular weight of 1,000 - 200,000.

The fiber of the invention is preferably prepared by impregnating or immersing a never-dried wet spun acrylic fiber with an aqueous solution of a water soluble polyamine, and heat treating the impregnated fiber at a temperature between 100 and 180°C. A textile article made from the deodorizing fiber of the invention in combination with a deodorizing fiber having an anionic functional group can remove an objectionable compound smell or odor in the ambient atmosphere.

(19)



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(54) **DEORORIZING FIBER, PROCESS FOR PREPARING THE SAME, AND DEODORIZING FIBER PRODUCT**

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**JP-A- 8 074 177**

- **PATENT ABSTRACTS OF JAPAN vol. 011, no. 369 (C-461), 2 December 1987 (1987-12-02) & JP 62 141128 A (KANEBO LTD), 24 June 1987 (1987-06-24)**

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**Description**

**[0001]** This invention relates to a deodorizing fiber a method of producing said fiber and a textile comprising the fiber.

5 **Background Art**

**[0002]** In recent years, comfortable living environments have become the object of attention. There have been known many attempts for removing offensive smells present in various environments, for examples, in a living room, in a vehicle and even in a refrigerator.

10 **[0003]** Among the attempts, special attention has been focused on deodorizing tobacco smoke smells present in an office, in a living room and in automobile on account of the penetration of anti-smoking movement.

**[0004]** Some deodorants utilizing amine compounds for removing tobacco smoke smells have already been proposed. For example, an acrylic woven fabric containing a deodorant carrying a polyethylene-imine and nonionic moisture absorbing organic substances has been disclosed in Japanese Unexamined Patent Publication (Kokai) No. 15 3-146064.

**[0005]** However, it has been found that the proposed fabric does not provide a satisfactory characteristics pertaining to durability to washing and to processability.

20 **[0006]** A material for a tobacco smoke filter in which a reactive group is introduced into a cellulosic molecule to be reacted with a polyethylene-imine is disclosed in Japanese Unexamined Patent Publication (Kokai) No. 57-16687. The proposed product produces a localized formation of bonded reacted polyethylene-imine and the bonded polyethylene-imine is readily stripped off.

**[0007]** Further more, Japanese Unexamined Patent Publication (Kokai) No. 62-141128 describes a deodorizing synthetic acrylic fiber and a process for producing the same in which an amino group-introduced metal porphyrin was incorporated in the wet-gel fiber (undried fiber) in a manufacturing process stage of an acrylic fiber in order to improve 25 fastness to washing, and the fiber was subsequently dried to produce a deodorizing densified fiber. Although the deodorizing characteristics of the synthetic acrylic fiber according to the proposed method exhibits a satisfactory fastness to washing, the fiber is not durable to dyeing. In the patent publication, it is described that a polyvinyl amine which is a polyamine is chemically bonded to metal porphyrin. In this case, since the polyvinyl amine and the metal form a water-insoluble complex-compound, it is hardly possible to apply the compound in the form of a solution to a fiber 30 because the polyvinyl amine and the metal form an complex which is insoluble in water. It is natural that the complex adheres only to surface of fiber. Accordingly, the resultant textile products lacks fastness to dyeing.

**[0008]** As methods for improving dyeability, chemical incorporation of an amine compound to a fiber substrate has been known in the art. The methods include, for example, copolymerization of fiber forming polymer (Japanese Examined Patent Publications (Kokoku) No. 47-15096, No. 47-32157, No. 48-30479 and No. 55-6725), application of 35 graft polymerization to as-spun fiber after fiber forming process (Japanese Patent Publication (Kokoku) No. 38-8218, No. 47-23988 and No. 37-15415), polymer blending technique (Japanese Patent Publications (Kokoku) No. 38-20972 and No. 37-2997), direct application of impregnation method to fiber (Japanese Examined Patent Publications (Kokoku) No. 29-8215, No. 47-23988 and No. 48-23834) and the like.

40 **[0009]** In any of these known methods, amine compounds incorporated in fibers are preferably in the form of a salt according to the descriptions of publications. The fibers according to these known methods lack the capability of deodorizing offensive smells from an acid compound and/or a compound containing carbonyl groups which is a source of an offensive smell.

**[0010]** Japanese Examined Patent Publication (Kokoku) No. 22673 describes a cleaning filter in which a plurality of carrier substrates each impregnated with different components capable of deodorizing a plurality of different kinds of 45 unpleasant smells are compounded. Textile articles in which a carried deodorant is adhered to the surface of a fiber by coating or impregnation, feel stiff to the hand. Since the deodorant component is readily stripped off when the articles are washed or dyed, these textile articles cannot be used for clothing, interiors and furnishings where fastness to washing and dyeing or fashionable qualities are required.

**[0011]** In a textile article using a deodorizing fiber, it is generally required that the deodorizing characteristics of the fiber should be fast or durable against washing and dyeing processes. With a view extending the end-use field of a deodorizing fiber, dyeing of deodorizing fiber is strongly required as in conventional fibers. The deodorizing characteristics of deodorizing fiber should be retained even after the fiber has been dyed. In other words, durability of deodorizing characteristics to dyeing property is extremely important requirement in a dyed deodorizing fiber.

55 **[0012]** The fastness to washing referred to herein is defined as a retention degree (preservation degree) of the original characteristics of a textile article after washing in which a deposit adhered to the fiber prior of washing has been stripped off (removed) by both mechanical and chemical actions of flowing washing water in the presence of a minimum surfactant which does not deteriorate physical characteristics and does not change the color of the textile article. Washing is a treatment applied to with a view to stripping off the deposit or the adherent which is generally

bonded by means of physical adsorption (Washing Test Method is described in JIS-L-0217.).

**[0013]** On the other hand, the fastness to dyeing as herein referred to is defined as a retention degree of the original characteristics of a fiber after dyeing in which a deposit adhered to the fiber prior to dyeing has been stripped off (removed) under heat at dyeing by a strong thermodynamic action, and the property indicates an occurrence of stripping-off of physically adsorbed deposit and ionically bonded adduct. Retention of deodorizing characteristics towards unpleasant smells after the deodorizing fiber has been dyed has been a very serious problems to deal with.

#### Disclosure of the Invention

**[0014]** The object of the present invention is, in a broad sense, to provide a deodorizing fiber and a textile article with durable deodorizing characteristic.

**[0015]** A specific object of the invention is to provide a deodorizing fiber and textile article with deodorizing characteristics exceedingly durable against various treatments, for example, washing and dyeing to which a conventional fiber or textile article is subjected.

**[0016]** A more specific object of the invention is to provide a fiber material having excellent deodorizing characteristics which will not be lost under routine treatments applied during use.

**[0017]** A further object of the invention is to provide durable textile articles exhibiting deodorizing effect on a broad spectrum of unpleasant smells.

**[0018]** This invention provides a deodorizing fiber as defined in claim 1.

**[0019]** The acid group as herein referred to is the acid group contained inherently in the substrate forming fiber, that is a carboxyl group or sulfonic group which can be reacted with the amino group containing compound.

**[0020]** The substrate fiber pertaining to the invention is an organic fiber and includes natural fibers, chemical fibers and synthetic organic fibers. Representative examples for natural fibers are cotton and wool. The chemical fibers include regenerated cellulose fibers such as viscose rayon, cuprammonium rayon and a fiber formed by means of chemical modification of natural cellulosic materials, for example, acetate fiber. The synthetic organic fibers are made from fiber forming organic synthetic polymers. Representative examples of the fibers are polyamide fiber, acrylic fiber, polyester fiber, or the like.

**[0021]** In the case where these fibers do not have any acid group in themselves, a modifying compound having acid groups is incorporated or introduced into the fibers by means of addition bonding or alternatively they can be used as substrate fiber after they have been treated with a suitable modifier to make a fiber containing a prescribed amount of acid groups.

**[0022]** In the case where the fibers are synthetic organic polymeric fibers, the acid groups are introduced during the preparation of the polymer by means of copolymerizing a prescribed amount of a copolymerizable monomer, and a fiber containing acid groups in a proportionate amount of 0.01 - 2.5 mole/kg fiber can be easily prepared by applying a known spinning and stretching process to the obtained copolymer.

**[0023]** In the invention, acrylic fiber can be used as the most preferred fiber substrate for the purpose because the fiber is made from copolymer containing a prescribed amount of acid groups which can be readily prepared in the manner as mentioned above.

**[0024]** In the invention, the amino group is a salt-unsubstituted amino group of which introduction into the fiber is made by chemically bonding a polyamine having a molecular weight of 1,000 - 200,000 with fiber and held firmly on the fiber. A salt-substituted amino group is an amine neutralized by an acid, for example, an amino sulfate and a chloride of amino hydrochloric acid. It cannot absorb smells emitted from a carbonyl group-containing compound and an acid compound up to a satisfactory level, and cannot make a fiber having a fast deodorizing effect.

**[0025]** The deodorizing fiber according to the invention has an amino group bonded firmly on the fiber in which the amino group is chemically bonded to 50 - 100 mol%, preferably 60 mole% or more of the acid groups contained in the fiber. Since the deodorizing fiber of the invention carries a sufficient amount of amino group bonded chemically to the acid group in the fiber substrate, a remarkable removal of unpleasant acid smells emitted from aldehyde and sulfide can be effected and the deodorizing characteristics of the fiber becomes durable against physico-chemical actions encountered during dyeing and washing.

**[0026]** It is, however, noted that a deodorizing effect cannot be attained in case where the amount of amino groups present in the fiber is relatively small as compared with a relatively larger amount of acid groups present in the fiber substrate. Accordingly, an application of greater amount of amino groups is required so as to maintain the presence of free amino groups in the fiber because the free amino groups effect deodorizing.

**[0027]** The deodorizing fiber according to the invention can be prepared by a process according to claim 5.

**[0028]** In the process, the concentration of a treating or immersing bath of the water soluble polyamine can be optionally selected as far as the prescribed amount of water soluble polyamine compound can be attached to the fiber. The amount of water-soluble polyamine compound attached to the fiber can be determined on the basis of a pick up ratio or a squeezed solution ratio.

**[0029]** When the heat treatment is carried out under moist or wet heat or steam, the deodorizing characteristics of fiber becomes fast to dyeing and washing. When the deodorizing fiber is an acrylic fiber, deodorizing fastness of the fiber to treatments such as washing and dyeing can be further enhanced by a process comprising impregnating a never-dried fiber (hereinafter, the fiber may be referred to as undried fiber.) with a polyamine compound in which the never-dried fiber is a fiber immediately after stretching in forming an acrylic fiber in a wet spinning or gap-type wet spinning process.

**[0030]** The deodorizing fiber of the invention can be of either continuous fiber or staple fiber. When the fiber is chemical or synthetic fiber, it can be prepared in the form of a tow. The deodorizing fiber of the invention may be used in the form of yarn, and it is mostly converted into the form of woven fabric, knitted fabric or nonwoven fabric for making textile articles such as clothing or the like. In the textile goods as mentioned above, goods can be wholly composed of the fiber of the invention. The deodorizing fiber of the invention can be blended with a conventional fiber to make a textile article.

**[0031]** An durable deodorizing textile article which exhibits an extensive deodorizing characteristics capable of effecting extensive removal of compound smells having a wide smell spectrum covering acid compound-based smell and basic compound-based smell, can be attained by blending at least 5% by weight of a deodorizing fiber of the invention with at least 0.5% by weight of a fiber exhibiting a deodorizing characteristic towards a basic compound-based smell, especially a fiber containing anionic functional groups at a content of 0.2 - 10 mol/kg fiber or else a deodorizing fiber containing a transition metal at a content of less than 0.1 - 5 mol/kg fiber bonded to the anionic functional groups mentioned above.

**[0032]** The anionic functional groups contained in the fiber enabling to deodorize the basic compound-based smell as referred to herein, are sulfonic groups or carboxyl groups which can be introduced into the fiber substrate of natural fibers, chemical fibers or synthetic fibers by the same method as that method for introducing the acid groups as mentioned-above. A transition metal is introduced into the fiber by contacting the fiber containing the anionic functional groups as mentioned-above with an aqueous solution of a metal salt, for examples, a metal sulfate, a metal nitrate, and the like.

**[0033]** The mixed or blended fiber can be made into a final product in the form of a woven or knitted union fabric, a twisted plied yarn, a mixed knitted fabric, nonwoven by application of conventional converting means.

#### Best Mode of Carrying Out of the Invention

**[0034]** The acid groups contained in the deodorizing fiber of the invention are carboxyl groups or sulfonic groups, especially sulfonic group. The deodorizing fiber of the invention contains acid groups at a proportionate content of 0.01 - 2.5 mol/kg fiber, preferably 0.01 - 1.5 mol/kg fiber. When a proportionate content of acid groups is less than 0.01 mol/kg fiber, a satisfactory bond between an acid groups and a water-soluble polyamine cannot be attained and the water-soluble polyamine having amino groups may be readily stripped off from the fiber during dyeing and washing treatment. Accordingly, a proportionate content of less than 0.01 mol/kg fiber of acid groups cannot be used in the invention. On the contrary, when a proportionate content of acid groups exceeds 2.5 mol/kg fiber, acid group-containing polymeric compound in the fiber become readily detached during dyeing and washing.

**[0035]** When a fiber does not contain acid groups, the acid groups can be introduced into the fiber by producing a prescribed amount of carboxyl groups in the fiber substrate by means of an addition of a chemical substance to the fiber substrate using a known method such as a graft polymerization, or by means of a chemical modification of the fiber using a chemical treatment such as oxidization. Such means for introducing acid groups can be used as a method for preparation of a fiber containing a prescribed amount of carboxyl groups from wool, cotton, a regenerated cellulose fiber and a cellulose acetate fiber.

**[0036]** Introduction of a prescribed amount of acid groups into a synthetic organic fiber can be easily made with use of a copolymer prepared by copolymerizing a comonomer having a prescribed amount of acid groups by applying a known suitable spinning and stretching method for the copolymer.

**[0037]** For both of a condensation polymerized copolymer pertaining to polyamide fibers and polyester fibers and a addition polymerized polymers pertaining to acrylic fibers, preparations of the respective fiber forming polymers containing a prescribed amount of acid groups by an addition of comonomer having carboxyl or sulfonic groups can be practiced using a conventionally known method.

**[0038]** Acrylic fibers are suitable fibers for preparation of fibers containing carboxyl or sulfonic groups using a copolymerizing method, and are preferable fiber materials capable of providing a deodorizing fiber of the invention with the fiber substrates because the method for forming the fibers from a copolymer having a prescribed amount of carboxyl or sulfonic groups as well as the properties of the fibers are not substantially different from a conventional acrylic fiber.

**[0039]** Examples of acrylic synthetic fibers constituting a deodorizing acrylic fiber of the invention are copolymeric fibers obtained by copolymerizing 30% or more by weight of acrylonitrile with one or two or more vinyl monomers including acrylic acid, methyl acrylate, ethyl acrylate, itaconic acid, methacrylic acid, styrene, acryl amide, methacryl

amide, vinyl acetate, vinyl chloride, vinilidene chloride, metharyl sulfonic acid, a salt of metharyl sulfonic acid, styrene sulfonic acid, a salt of styrene sulfonic acid, aryl sulfonic acid, a salt of aryl sulfonic acid and the like.

**[0040]** In the invention, especially preferred acrylic fibers are fibers made of copolymers obtained by copolymerizing 80% or more by weight of acrylonitrile with one or two or more of vinyl monomers including acrylic acid, methyl acrylate, methyl methacrylate, acryl amide, vinyl acetate, vinyl chloride, a salt of metharyl sulfonic acid, a salt of styrene sulfonic acid and the like.

**[0041]** It is necessary that a deodorizing fiber of the present invention contains amino groups in a proportionate content of 0.03 - 3.0 mol/kg fiber, preferably 0.05 - 2 mol/kg fiber. When the content becomes less than 0.03 mol/kg fiber, absorption characteristics of the fiber towards unpleasant smells from a carbonyl group-containing compound and an acid compound are lowered. When the content exceeds 3 mol/kg fiber, handling touch of the fiber becomes worse.

**[0042]** It is noted that the polyamine compound in the fiber is fixedly held by the bond between the acid groups and the amino groups. A polyamine compound having a molecular weight of 1,000 - 200,000 is used.

**[0043]** In a deodorizing fiber according to the invention, a selective use of polyamine for introducing amino group is preferably made of a water-soluble polyamine having more than two functional group which is not substituted by salt. Examples of water-soluble polyamine compounds include ethylene diamine, diaminopropyl amine, 2,2'-azo-bis-(2-amizino propane), carbohydrazine, thiocarbonyhydrazide, thiosemihydrazide, thiourea, guanidine salts, guanylurea salts, 1,4-diaminobutane, diamiopropane, diaminomaleonitrile, spiroacetal compounds, dodecanediohydrazide, hexamethylene diamine, stearic acid diethylene amine, xitothane, polyethylene-imine, polyaryl amine, amino-modified acrylic polymers, and the like. These compounds may be used alone or in combination of more than two compound thereof.

**[0044]** In the invention, an impregnation or immersion treatment with the amine compounds can be carried out by means of an aqueous solution or aqueous emulsified dispersion. Use of a water-soluble polyamine is preferred. This is because the treatment bath composed of aqueous solution is stable with the use of water, and because a firm linking bond between the amino group and the acid group as well as a high bond ratio therebetween is successfully attained with the use of a water-soluble amine compound. When use is made of a polyamine compound which is not water-soluble, the bond ratio obtainable is somewhat lowered.

**[0045]** Use of a water-soluble polyamine compound having a molecular weight ranging from 1,000 to 200,000 is especially preferred. When the molecular weight is less than 1,000, the bond ratio per pair of the molecular chain constituting acrylic fiber and the molecular chain constituting a water-soluble polyamine compound becomes low so that the water-soluble polyamine compound becomes detached since breakage of the bond occurs easily during dyeing treatment. Accordingly, the molecular weight less than 1,000 cannot be utilized. A molecular weight exceeding 200,000, is not preferred because hand touch of fiber or texture becomes deteriorated. Further, in such high level of molecular weight, a cohesion of the treated fiber may occur since the water-insoluble compound is fixed on the surface of fiber due to poor migration or poor permeation of the compound. Specifically, use of one or two or more compounds selected from a polyethylene-imine, polyaryl amine, amino-modified acrylic polymer is preferable. However, it is noted that a mixed use of a water-soluble polyamine compound with a metallic compound or a metal ion causes the treated fiber to deteriorate in deodorizing fastness in consequence due to formation of a metal complex which is insoluble in water.

**[0046]** In a deodorizing fiber of the invention, a bond ratio of a polyamine compound to the acid groups is preferably from 50 - 100 mol%, especially 60 - 100 mol%. When the bond ratio of acid groups is less than 50 mol%, the fiber has a poor deodorizing fastness and is not durable against dyeing treatment.

**[0047]** The bond ratio for acid groups can be given based determination of the sum of acid groups in a fiber and the determination of amount of remaining acid groups (hereinafter called as amount of remaining acid groups) which is not bonded to the functional groups in a polyamine by the following formula:

$$\text{Bond ratio of acid groups (mol\%)} = \frac{\text{(sum of amount acid groups - amount remaining acid groups)}}{\text{sum of acid groups}} \times 100$$

$$= \frac{\text{(sum of amount acid groups - amount remaining acid groups)}}{\text{sum of acid groups}} \times 100$$

**[0048]** A deodorizing fiber of the invention can be prepared by a method comprising contacting a fiber having a prescribed amount of acid groups with a water-soluble polyamine to be impregnated; subsequently heat treating the impregnated fiber to bind the amino group in the water-soluble polyamine to 70 - 100% of the carboxyl or sulfonic groups so that the residual polyamine compound having amino groups is fixedly held on the fiber substrate. The heat treatment can be carried out in a dry heat atmosphere at an ambient temperature of 100°C or more. But this method of heat treatment is time consuming, heat treatment by a wet heat condition may be preferred. A wet heat treatment

condition used herein, is carried out in a pressurized steam at a temperature of 100°C - 180°C, preferably at a temperature of 105°C - 130°C for from about 30 seconds to 10 minutes. A temperature of the pressurized steam of less than 100°C cannot be used in the invention because a sufficient level of bond between a polyamine compound containing amino groups and the acid groups in the fiber cannot be promoted consequentially causing the amine compound containing amino group to be readily detached (stripped off) during washing in the final product. A temperature of steam exceeding 180°C cannot be used because a remarkable deterioration of hand touch of the product fiber may result.

[0049] The contacting the fiber with a water soluble-amine compound can be carried out by immersing the fiber in an aqueous solution of the water-soluble polyamine compound and subsequently squeezed to remove an excessive liquid. In the treatment, a concentration of the water-soluble polyamine in the aqueous solution ranges from about 0.01-about 20% by weight, although the concentration is varied depending on conditions of immersion and squeezing in a specific operation. The amount of impregnation is adjusted at 0.05 - 10% by weight based on the weight of fiber by means of dehydration using a mangle or centrifuge. Temperature of the aqueous solution at the immersion may be optionally selected. An operational mode of heat treatment may be determined in accordance with the dimensional (shape) form of fiber and carried out using a conventional apparatus available at textile processing plant. In the case where the fiber is a continuous goods, for example, in the form of tow, woven fabric, knitted fabric and nonwoven fabric, the textile goods subsequent to dipping and padding is suitably heat treated by application of a tenter or steamer, tow-reactor, moist heat treating machine with cross-wise spreader. In the case where textile goods is a final textile article such as sweater and the like, the heat treatment can be carried out using a batch-wise drier, a tumble drier, or a wet heat tumbling machine.

[0050] It is noted that the fiber subsequent to heat treatment should be washed for removal of an excessive polyamine compound adhered to the fiber.

[0051] In the case where the fiber is an acrylic fiber, an especially preferred method for impregnation of a water-soluble polyamine compound to the fiber is carried out by contacting the water-soluble polyamine compound with the fiber in a never-dried state (frequently called as wet-gel fiber) in which a consequent fiber in a suitable stretching subsequent to a wet-spinning of the fiber has never been dried. A never-dried fiber as herein referred to means an acrylic fiber in an aqueous swollen state (undried fiber) before the acrylic fiber structure becomes irreversibly densified by drying and an acrylic fiber having an initial swelling degree (Qc) of 50 - 250% by weight, preferably 60 - 200% by weight; the initial swelling degree is defined below:

$$Qc (\%) = (W_1 - W_2)/W_2 \times 100$$

[0052] (In the formula,  $W_1$  represents a weighings (g) of a specimen weighing several grammes of a fiber which has never been dried, centrifuged at 900G at 25°C for 5 minutes, and  $W_2$  represents a weighings of the specimen . after drying at 105°C for 2 hours.)

[0053] A decrease in residual acid group and a degree of bond for a acid group are attained when a heat treatment at a dried conditions is carried out after a water-soluble polyamine was impregnated to an undried acrylic fiber. Further decrease in the residual acid group and increase in degree of bond of the acid group are attained when a steam treatment is carried out after the heat treatment. This is because an ionic intermolecular cross-linking reaction between the acid group in the cross section of acrylic fiber and the amino group in water soluble polyamine is promoted by the moist heat treatment. Such function of the undried fiber is specific to acrylic fiber and cannot be presented by various cellulosic fibers, polyamide fibers and polyester fibers.

[0054] The deodorizing fiber of the invention prepared in accordance with the manner as the above-mentioned is a fiber which exhibits deodorizing effect in virtue of the presence of amino groups, and the fiber, as a raw material for making textile goods, can be used singly or in combination with other conventional textile fiber materials to produce end-use textile articles in every shape required through application of every conventional converting method.

[0055] Combining with an anionic group-type deodorizing fiber (hereinafter referred to as deodorizing fiber (B)), preferably with a deodorizing fiber which exhibits deodorizing characteristic towards tobacco smoke smell, the deodorizing fiber (hereinafter referred to as deodorizing fiber [A]) of the present invention can make an extensive deodorizing textile product having a deodorizing characteristics towards a broad smell spectrum.

[0056] As methods for combining a deodorizing fiber [A] with a deodorizing fiber [B], blend spinning, combination of filament yarn, twisted union yarn, union cloth wearing plaited knitting, or the like can be enumerated. With use of these methods, converted textile goods having a broad deodorizing spectrum in a various forms, for examples, yarns or thread, woven fabric, knitted fabric and nonwoven fabric can be produced for a variety of end-uses.

[0057] A fiber composition constituting these textile goods contains, as in combination, at least 5%, preferably at least 10% by weight of deodorizing fiber [A] and at least 0.1%, preferably at least 1% by weight of deodorizing fiber (B). The composition may contain other conventional fiber as a blending component. Accordingly, with the use of the blend of the fibers as mentioned-above, a textile article in end-use can remove not only smells emitted from carbonyl

compounds by virtue of deodorizing fiber [A], but also smells from basic compounds by virtue of deodorizing fiber [B], and can exhibit a durable deodorizing performance towards a compound smell.

**[0058]** A converted textile article can be made of a deodorizing fiber of the present invention and a deodorizing blend of fibers.

**[0059]** An anionic functional group of a deodorizing fiber [B] is a carboxyl group or sulfonic group and the content in the fiber is 0.2 - 10 equivalents/kg, preferably 0.4 - 5 equivalents/kg. When a content of carboxyl group is less than 0.2 equivalents/kg, a little deodorizing effect is obtained. A content of carboxyl group exceeding 10 equivalent/kg in the fiber is not preferred because moisture and water absorvencies of the fiber becomes excessively increased and because dimensional (shape) stability and deodorizing fastness of the fiber to washing as well as hand touch of fiber deteriorate.

**[0060]** Carboxyl group and sulfonic group may be contained either singly or concurrently. when an introduction of a greater amount of anionic functional group is required, carboxyl group is preferred since the carboxyl group, which excels sulfonic group in modifying characteristics can be introduced easily. A transition metal can be incorporated with anionic functional group in order to widen kinds of removable smells and in order to enhance deodorizing characteristics.

**[0061]** An anionic functional group, for an example, carboxyl group, can be introduced into fiber by the following methods enlisted by way of examples: a method in which graft polymerization of, for an example, acrylic acid is carried out utilizing for examples, amide group, amino group, and hydroxyl group in the fiber substrate; a method in which, for example, an acrylic fiber is hydrolysed; a method in which a polymer having carboxyl group, for example, acrylic acid is prepared by copolymerizing or by polymer blending. In a further example, the anionic functional group may be introduced by immersing a fiber which is in a never-dried state, obtained immediately after wet spinning into an aqueous solution of the above mentioned polymer, and drying the immersed fiber.

**[0062]** Transition metals as herein referred to includes copper, zinc, iron, nickel, chrome, cobalt and the like, and is introduced into fiber, for example, by immersion technique using a transition metal compounds such as copper compounds ( $\text{CuSO}_4$ ,  $\text{Cu}(\text{NO}_3)_2$  and the like), zinc compounds ( $\text{ZnSO}_4$ ,  $\text{Zn}(\text{NO}_3)_2$  and the like), iron compounds ( $\text{FeSO}_4$ ,  $\text{Fe}(\text{NO}_3)_2$  and the like), nickel compounds ( $\text{NiSO}_4$ ,  $\text{Ni}(\text{NO}_3)_2$  and the like), chromium compounds ( $\text{CrSO}_4$ ,  $\text{Cr}(\text{NO}_3)_2$  and the like), cobalt compounds ( $\text{CoSO}_4$ ,  $\text{Co}(\text{NO}_3)_2$  and the like) and the like. In view of that a remarkable deodorizing is attained, use is made of a copper compound or a zinc compound. A preferred content of a transition metal compound is 0.2 - 10 equivalents/kg fiber, the most preferred is 0.2 - 3 equivalents/kg fiber. When the content is less than 0.2 equivalents/kg fiber, a little deodorizing is obtained. When the content exceeds 10 equivalent/kg fiber, deodorizing effect towards ammonia deteriorates because the content of anionic groups becomes a little.

**[0063]** Deodorizing fiber [B] does not decrease in its deodorizing effect even when the fiber is used in blend with cellulosic fiber, acrylic fiber, polyamide fiber, a known deodorizing fiber, or an anti-fungal fiber.

### Examples

**[0064]** The invention will be described in more detail by way of the following Examples. The following Examples, however, are not intended to limit the scope of the invention.

**[0065]** The following are methods of various measurements and evaluations as referred to in the examples.

#### I. Method for evaluation of raw fiber materials

##### (1) washing Test:

**[0066]** Washing test was carried out in accordance with the method described in JIS-L-0217-Method 103.

##### (2) Measurement of residual acid group:

**[0067]** 1g of a sample fiber was immersed in 300 ml of an aqueous solution of sodium chloride having a concentration of 10% by weight and the immersion was shaken in a constant temperature bath at 40°C for 30 minutes. Then, the fiber was, subsequently washed sufficiently with a refined water and dried at 80°C for one hour to prepare a fiber retaining a sodium substituted acid group. The fiber was then treated with in a mixture solution composed of 5 ml of 98% sulfuric acid, 40 ml of 62% nitric acid and 2 ml of 70% perchloric acid on an electricity heater for 5 hours so that wet-decomposition was carried out. The resultant liquid was then diluted by 100 times with a refined water to prepare a dilution for a quantitative estimation of sodium by means of flame spectrum analysis. Quantity of retained acid group was determined using the quantity of the sodium determined by the analysis.

## (3) Evaluation of durability to dyeing of a deodorizing fiber:

**[0068]** A fiber was dyed with Kayanol Milling Blue BW (trade name of an acid dye available from Nippon Kayaku Co. Ltd.; C.I. Acid Blue 138) 3% owf in the presence of Migregal 2N 3% owf as a levelling agent and 0.2 cc/L of 90 weight % aqueous acetic acid solution for pH adjustment at a bath ratio of 1:80 at 100°C for 60 minutes. The dyed fiber was soaped in 1.0 weight % aqueous ammonium solution for 10 minutes to obtain samples for various tests.

## (4) Determination of absorption of an unpleasant smelling substance:

**[0069]** For determination of absorption of an unpleasant smelling substances by a fiber stock, 1.0g of a fiber sample was encapsulated in a Tedlar bag having a volume of 1,000 ml into which a unpleasant smelling substance was introduced together with 600 ml of air cleaned by passing through an active carbon filter and concentration of remaining gas in the Tedlar bag after 60 minutes was determined by using a gas detecting tube to find the quantity of absorbed unpleasant smelling substance. The unpleasant smelling substances used consisted of an aqueous solution containing of 0.04% by weight of acetaldehyde as a representative compound containing carbonyl compound and 10 ml of a gas containing 2,000 ppm of hydrogen sulfide as an acid substance.

## II. Evaluation of a deodorizing textile article made of a blended spun yarn:

## (1) Washing test:

**[0070]** Washing test was carried out in accordance with JIS-L-0217-Method 103.

## (2) Deodorizing characteristics towards a bad-smelling substance

**[0071]** 1g of a fiber was encapsulated together with 600 ml of a bad smelling composition in a Tedlar bag and the concentration of the remaining gas was measured using Kitagawa gas detecting tube after 60 minutes. The initial concentrations of the unpleasant smelling components in the unpleasant smelling composition were 100 ppm of acetaldehyde as a carbonyl compound, 40 ppm of acetic acid as an acid compound, 140 ppm of trimethylamine and 140 ppm of ammonia.

## (3) Evaluation of hand touch of a converted textile article:

**[0072]** Evaluation of hand touch for a textile article was performed by a panel consisting of 5 persons. Rating of sensory evaluation was determined by the sum of ratings given by each member of the panel on a sample according to the standard criteria given below:

| Hand touch     | Value of rating |
|----------------|-----------------|
| Not stiff      | 3               |
| Slightly stiff | 2               |
| Stiff          | 1               |

## (4) Evaluation of deodorizing characteristics on a tobacco smoke

**[0073]** Sensory evaluation of deodorizing characteristics on a tobacco smoke was performed by a panel consisting of 16 persons. Rating of evaluation was determined on a sample by the sum of ratings given by each member of the panel according to the standard criteria given hereinafter.

**[0074]** A by-stream of smoke emitted during smoking of a piece of cigarette Mild Seven® (a product of Japan Tobacco Company) was collected for a period of 10 minutes into a Meyer flask having a volume of 2 liters. Using a syringe, 0.5 ml from the collected smoke was introduced into a Mayer flask having a volume of 600 ml. Then, 1g of each sample fiber was introduced into the flask. After the sample fiber had been left standing for two hours, the smell within the flask and the smell of the fiber itself were rated by means of perceptions of each member of the panel according to the standard criteria given below:

| Ratings by human perception: | Ratings |
|------------------------------|---------|
| No effect perceptible        | 1       |

(continued)

| Ratings by human perception: | Ratings |
|------------------------------|---------|
| Almost perceptible           | 2       |
| Slight effect is perceptible | 3       |
| Fair effect is perceptible   | 4       |

[Examples 1 - 8, Comparative Example 1]

**[0075]** 94.5% by weight of acrylonitrile, 5.0% by weight of methyl acrylate and 0.5% by weight of sodium methacryl sulphonate were copolymerized to obtain a copolymer. A spinning dope containing 15.5% by weight of the polymer was prepared by dissolving the copolymer in 70 weight % nitric acid.

**[0076]** The spinning dope was spun in a nitric acid based coagulating bath containing 37% by weight of nitric acid kept at 0°C through a spinneret with fine holes having a diameter of 0.06 mm in the form of tow, and the tow was subsequently stretched 9 times in a boiling water bath after washing to obtain a undried fiber. The sulfonic acid group content in the fiber was found 0.056 mole/kg fiber.

**[0077]** The undried fiber was treated by immersing in aqueous solutions (20°C) of polyethylene-imine (manufactured by Nippon Shokubai Company Ltd.) having a degree of polymerization of 1630 (molecular weight about 70,000). The immersion was carried out for 1 minute and subsequently was dehydrated at a pick-up of 80% by weight. The concentrations of the polyimine in the immersing solutions were 1.3% by weight (Example 1), 2.5% by weight (Example 2), 3.8% by weight (Example 3), 6.3% by weight (Example 4) and 12.5% by weight (Example 5). After dehydration, the dipped fibers were dried at 80°C for a hour, and were subjected to wet-heat (moist heat) treatment for 5 minutes in a saturated steam at 120°C in an autoclave to obtain the fibers of Examples 1 through 5.

**[0078]** For Comparative Example 1, an immersion treatment of the polyethylene-imine aqueous solution was carried out in a similar manner in Example 2, in which the polyethylene-imine aqueous solution was brought at pH 4 by an addition of phosphoric acid to be substituted by a phosphate of polyethylene-imine having a polymerization degree of 1630 (molecular weight 70,000) to prepare a comparative fiber. The obtained fibers, fibers after ten times of repeated washings and the dyed fibers were tested on absorption of offensive smell substances. The results of the tests and bond ratios of acid groups are summarized in Table 1.

[Examples 6, 7]

**[0079]** A fiber (Example 6) was prepared by a modified process according to Example 2 excepting the wet heat treatment.

**[0080]** Replacing the wet heat treatment in Example 2 for treatment by a saturated steam at 190°C for 5 minutes, Example 2 was repeated to obtain the fiber of Example 7.

**[0081]** The obtained fiber (Example 7) and the fiber after 10 times of repetition of washing and the fiber after dyeing were tested on the absorption of offensive smell substances. The results and bind ratios of acid group are tabulated in Table 1.

[Example 8]

**[0082]** The undried fiber as used in Example 1 was dehydrated and was dried for 1 hour. The dried fiber was then wet heat treated in an autoclave with a saturated steam at 120°C for 5 minutes and was subsequently treated by immersing in an aqueous solution containing 12.0% by weight of a polyethylene-imine having a molecular weight of 70,000 at a temperature of 20°C for 1 minute, and finally dehydrated at a pick-up of 17 weight %. The treated fiber was dried at 80°C for 1 hour to obtain the fiber of Example 8.

**[0083]** The obtained fiber, the fiber after 10 times of repetition of washing and the fiber after dyeing were tested on the absorption of offensive smell substances. The results and bind ratios of the acid group are tabulated in Table 1.

|                       | Amine Compounds                     |                   | Bond ratio of acid group | Deodorizing characteristics of fiber |                  | Deodorizing characteristics of fiber after 10 repetition of washing |                  | Deodorizing characteristics of fiber after dyeing |                  | Adhesive cohesion of fibers |  |
|-----------------------|-------------------------------------|-------------------|--------------------------|--------------------------------------|------------------|---|------------------|---|------------------|-----------------------------|--|
|                       | Content of amino group mol/kg fiber | Salt-substitution |                          | Aldehyde                             | Hydrogen sulfide | Aldehyde  | Hydrogen sulfide | Aldehyde  | Hydrogen sulfide |                             |  |
|                       |                                     |                   |                          | mg equivalent/kg fiber               |                  | mg equivalent/kg fiber  |                  | mg equivalent/kg fiber                            |                  |                             |  |
| Example 1             | 0.06                                | none              | 70                       | 2.0                                  | 0.5              | 1.4   | 0.3              | 1.2   | 0.5              | none                        |  |
| Example 2             | 0.12                                | none              | 83                       | 3.6                                  | 0.6              | 2.9   | 0.5              | 2.5   | 0.5              | none                        |  |
| Example 3             | 0.18                                | none              | 92                       | 4.5                                  | 0.7              | 3.3   | 0.5              | 3.0   | 0.5              | none                        |  |
| Example 4             | 0.30                                | none              | 93                       | 4.5                                  | 0.7              | 3.8   | 0.7              | 3.4   | 0.7              | none                        |  |
| Example 5             | 0.60                                | none              | 93                       | 4.5                                  | 0.7              | 4.5   | 0.7              | 3.5   | 0.7              | none                        |  |
| Comparative Example 1 | 0.18                                | done              | 5                        | 0.5                                  | 0.1              | 0.9   | 0.2              | 0.1   | 0                | none                        |  |
| Example 6             | 0.12                                | none              | 32                       | 3.6                                  | 0.6              | 0.7   | 0.1              | 0.6   | 0.2              | none                        |  |
| Example 7             | 0.12                                | none              | 92                       | 3.6                                  | 0.6              | 0.2   | 0.1              | 2.1   | 0.4              | observed                    |  |
| Example 8             | 0.18                                | none              | 5                        | 4.0                                  | 0.7              | 0.7   | 0.2              | 0.7   | 0.1              | none                        |  |

**[0084]** As clearly shown in Table 1, the fibers according to Examples 1 - 5 exhibit excellent deodorizing characteristics towards acetaldehyde and hydrogen sulfide smells even after the fibers were subjected to 10 times of repeated washing treatments or to dyeing process. In contrast, the fiber according to Comparative Example 1 has a lower acid group bond ratio in comparison with the fiber according to Examples 2 at the same level of the build up, and the ratio of fall in the deodorizing characteristics towards acetaldehyde and hydrogen sulfide smells of the fiber subjected to ten times of repeated washing (and dyeing process) relative to that of the fiber prior to the washing (and the dyeing process) was greater in comparison with the ratio of fall for the fiber according to Example 2.

**[0085]** The fibers obtained according to Examples 6 and 8 in which the fiber were heat treated after polyethylene-imine treatment. These fibers exhibit, regardless of conditions of heat treatments applied, exceedingly excellent deodorizing fastness to washing (to dyeing processing) than the fiber according to Comparative Example 1 does.

**[0086]** The fiber obtained according to Example 7 in which a treatment with a steam was applied to the fiber had an adherent cohesion between fibers.

[Example 9]

**[0087]** The undried fiber as used in Example 1 was immersed in an aqueous dispersion containing 6.3% by weight of a polyethylene-imine (Molecular weight is about 70,000.) and 10% by weight of phthalocyanine copper complex at 20°C for one minute and was subsequently dried at 80°C for 1 hour, and the dried fiber was then treated with a saturated steam at 120°C in an autoclave for 5 minutes to obtain a modified fiber. Absorption test of unpleasant smelling substances was carried out on the fiber as obtained, the obtained fiber after 10 repetition of washing and the obtained fiber as dyed. The results obtained are summarized together with acid group bond ratio in Table 2.

[Examples 10 - 12, Comparative Example 2]

**[0088]** A carboxymethyl cellulose fiber containing carboxyl group in a ratio of 1.85 mol/kg fiber was treated by immersing aqueous solutions of xithothane at 20°C for a period of 1 minute; the solutions contain chitosan 0.3% by weight (Comparative Example 2), 5.0% by weight (Example 10), 10.0% by weight (Example 11) and 30% by weight (Example 12) respectively. The immersions were squeezed at a pick up ratio of 100% by weight to obtain the dehydrated fibers. After the dehydrated fibers were then dried at 120°C for 15 minutes, the dried fiber was then treated with a saturated steam at 120°C in an autoclave for 3 minutes to obtain a modified fiber. Absorption tests of unpleasant smelling substances was carried out on the fibers as obtained, the obtained fiber after 10 repetition of washing and the obtained fiber as dyed. The results obtained are summarized together with acid group bond ratios in Table 2.

{Table 2}

|                       | Amine Compound                      |                     | Bond ratio of acid group | Deodorizing characteristics of fiber |                  | Deodorizing characteristics of fiber after 10 repetition of washing | Deodorizing characteristics of fiber after dyeing |                  | Adhesive cohesion of fibers |
|-----------------------|-------------------------------------|---------------------|--------------------------|--------------------------------------|------------------|---|---|------------------|-----------------------------|
|                       | Content of amino group mol/kg fiber | Solubility in water |                          | Acetaldehyde                         | Hydrogen sulfide |   | Acetaldehyde                                      | Hydrogen sulfide |                             |
| Example 4             | 0.30                                | S                   | 93                       | 4.5                                  | 0.7              | 3.8   | 3.4   | 0.7              | none                        |
| Example 9             | 0.30                                | I                   | 8                        | 0.8                                  | 0.1              | 0.7   | 0.6   | 0.1              | observed                    |
| Example 10            | 0.31                                | S                   | 51                       | 2.2                                  | 0.6              | 1.8   | 0.9   | 0.3              | none                        |
| Example 11            | 0.62                                | S                   | 63                       | 2.5                                  | 0.6              | 2.5   | 1.3   | 0.3              | none                        |
| Example 12            | 1.89                                | S                   | 89                       | 4.5                                  | 0.7              | 4.5   | 1.8   | 0.4              | none                        |
| Comparative Example 2 | 0.02                                | S                   | 41                       | 0.2                                  | 0.1              | 0   | 0   | 0                | none                        |

\* Water-solubility of amine compound: S, water-soluble; I, water-insoluble

[0089] As seen from Table 1, regardless of the kind of amino group contained, the fibers containing amino groups at a concentrations of 0.3 - 1.89/kg fiber which were prepared according to Examples 9 - 12, have good deodorizing characteristics towards acetaldehyde and hydrogen sulfide smells over the fiber containing amino groups at a concentration of 0.02 mole/kg fiber according to Comparative Example 2, in reference to the fiber as obtained, the fiber subjected to ten times of repeated washing.

[Comparative Example 3]

[0090] A spinning dope containing 16% by weight of a polymer obtained by copolymerizing 79.0 by weight of acrylonitrile, 21% by weight of acrylic acid was prepared by dissolving the polymer in an aqueous nitric acid of which concentration was 75% by weight. The spinning dope was extruded into a nitric acid-based coagulating bath containing 25% by weight of nitric acid at 0°C through a spinneret having holes with a diameter of 0.06 mm and the coagulated fiber was subsequently stretched 8 times in a boiling water after being washed to obtain an undried fiber. The carboxyl content of the undried fiber was found 2.72 mole/kg fiber.

[0091] The undried fiber was immersed in an ethanol solution of a polyethylene-imine having a polymerization degree of 1,680 (molecular weight: 70,000) at a concentration of 2% by weight at 20°C for 3 minutes and was subsequently dehydrated at a pick up ratio of 150% by weight. After the dehydration, the fiber was dried at a temperature of 60°C for 60 minutes to obtain the fiber of Comparative Example 3. Absorption test of unpleasant smelling substances was carried out on the fiber as obtained, the obtained fiber as treated by 10 repetition of washing and the obtained fiber as dyed. The results are tabulated together with acid group bond ratios in Table 3.

[0092] The rate of change in weight of fiber after washing test was determined by the following formula

Rate of change in weight of fiber after washing

$$\text{test (\%)} = (W_1 - W_2)/W_1 \times 100$$

in which  $W_1$  represents the weight of dried specimen before the washing test and  $W_2$  represents the weight of the dried specimen after the washing test.

[Table 3]

|                       | Amino group content | Acid group content | Deodorizing characteristics of fiber | Deodorizing characteristics of fiber after 10 repetition of washing | Weight change of fiber after washing | Deodorizing characteristics of fiber after dyeing |
|-----------------------|---------------------|--------------------|--------------------------------------|---|--------------------------------------|---|
|                       | mol/kg              |                    | Acetaldehyde mg equivalent/kg fiber  | Acetaldehyde mg equivalent/kg fiber                                 | (%)                                  | Acetaldehyde mg equivalent/kg fiber               |
| Comparative Example 3 | 0.18                | 0.272              | 4.5                                  | 0.6   | 13.8                                 | 0.0   |
| Example 2             | 0.12                | 0.06               | 3.6                                  | 2.9   | 1.3                                  | 2.5   |

**[0093]** As seen in Table, the fiber of Comparative Example 3 which contained carboxyl group at a ratio of 2.5 mole/kg fiber or more, exhibited an elution under repetition of washing treatment and in consequence the deodorizing characteristic of the fiber towards acetaldehyde became extremely low after 10 repeats of washing or after dyeing treatment.

5 [Examples 13 - 17, Comparative Examples 4 - 3]

**[0094]** A copolymer obtained by copolymerizing 74.7% by weight of acrylonitrile, 25.0% by weight of vinylidene chloride and 0.3% by weight of sodium metharyl sulphonate was dissolved in dimethylformamide to prepare a spinning dope having a polymer concentration at 18% by weight. The spinning dope was, then, extruded through a spinneret with holes having a diameter of 0.15 mm into a dimethylformamide-based coagulating bath containing 75% by weight of dimethylformamide which was kept at 30°C. The obtained fiber was stretched 5 times in a dimethylformamide-based stretching bath containing 75% by weight of dimethylformamide and the stretched fiber was then stretched 1.2 times in a boiling water after washing. The obtained undried had a swelling degree of 95.3% by weight. The content of sulfonic groups in the fiber was found 0.10 mole/kg fiber.

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15 **[0095]** The fiber was immersed in aqueous solutions having a pH of 10 of a polyaryl amine having a molecular weight of about 30,000 at various concentrations; 0.03% by weight (Comparative Example 4), 0.15% by weight (Example 13), 0.5% by weight (Example 14), 3.0% by weight (Example 15), 5.0% by weight (Example 16), 10.0% by weight (Example 17) and 15.0% by weight (Comparative Example 5). The immersions were carried out at 25°C for 1 minute and the immersed fibers were dehydrated at a pick up of 100% by weight. After dehydration, the treated fibers was dried at a temperature of 80°C for 1 hour and were subsequently treated under wet heat using an saturated steam at 120°C to obtain the fibers of Examples 13 - 17 and Comparative Examples 4 - 5.

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25 **[0096]** The obtained fibers, the obtained fiber after 10 times of repeated washings and the obtained fibers as dyed were tested on absorption of unpleasant smell components. Results of the tests and bond ratios of acid group are shown in Table 4.

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[Table 4]

|                       | Amino group content mol/kg fiber | Solubility of amine | Bond ratio of acid group mol% | Deodorizing characteristic of fiber |                  | Deodorizing characteristics of fiber after 10 repetition of washing |                  | Deodorizing characteristics of fiber after dyeing |                  | Adhesive cohesion of fibers |
|-----------------------|----------------------------------|---------------------|-------------------------------|-------------------------------------|------------------|---|------------------|---|------------------|-----------------------------|
|                       |                                  |                     |                               | Acetaldehyde mg equivalent/kg fiber | Hydrogen sulfide | Acetaldehyde mg equivalent/kg fiber                                 | Hydrogen sulfide | Acetaldehyde mg equivalent/kg fiber               | Hydrogen sulfide |                             |
| Example 13            | 0.034                            | S                   | 51                            | 1.4                                 | 0.4              | 1.2   | 0.4              | 1.1   | 0.4              | none                        |
| Example 14            | 0.114                            | S                   | 63                            | 1.8                                 | 0.5              | 1.6   | 0.5              | 1.5   | 0.4              | none                        |
| Example 15            | 0.682                            | S                   | 85                            | 3.0                                 | 0.7              | 2.5   | 0.5              | 2.3   | 0.4              | none                        |
| Example 16            | 1.136                            | S                   | 87                            | 4.5                                 | 0.7              | 3.3   | 0.6              | 3.1   | 0.5              | none                        |
| Example 17            | 2.273                            | S                   | 93                            | 4.5                                 | 0.7              | 3.8   | 0.7              | 3.4   | 0.7              | none                        |
| Comparative Example 4 | 0.006                            | S                   | 12                            | 0.7                                 | 0.1              | 0.0   | 0.1              | 0.0   | 0.0              | none                        |
| Comparative Example 5 | 3.409                            | S                   | 93                            | 4.5                                 | 0.7              | 4.1   | 0.7              | 4.0   | 0.7              | observed                    |

\* Solubility of amine: Reference to solubility of amine. S refers to water-soluble, I, insoluble in water respectively.

**[0097]** As clearly shown in Table 4, in comparison with the fiber according to Comparative Example 4 in which the fiber contains the bonded amino group at a concentration of 0.006 mol/kg fiber, the fibers according to Examples 13 - 17 in which the fibers were brought to contain the bonded amino group in quantities of 0.034 - 0.27 mole/kg fiber by using aqueous solutions at pH 10 of polyaryl amine at pH 10 exhibited excellent deodorizing characteristics of the fiber towards acetaldehyde and hydrogen sulfide smells with reference to the fiber after ten times repetition of washing and the fiber after dyeing. The fibers according to these Examples produce no conglutination of fiber, whereas the fiber according to Comparative Example 1 in which the fiber contained the amino groups at a concentration of 3.41 mol/kg fiber produced an intense conglutination.

**[Examples 18 - 21]**

**[0098]** A polymer prepared by copolymerizing 94.6% by weight of acrylonitrile, 5.0% by weight of methyl acrylate and 0.4% by weight of itaconic acid was dissolved in 70 weight % nitric acid to obtain a spinning dope containing the polymer at a concentration of 16% by weight. The spinning dope was extruded into a nitric acid-based coagulating bath containing nitric acid at a concentration of 35% by weight kept at a temperature of 0°C, and the resultant coagulated fiber after washing was subsequently stretched 8 times in a boiling water to obtain an undried fiber. The undried fiber contained carboxyl groups in a quantity of 0.06 mole/kg fiber.

**[0099]** The undried fiber was immersed at 20°C for one minute in aqueous solutions of polyethylene-imine having a molecular weight of 70,000 in which the aqueous solutions contain the polyethylene-imine at a concentration of 1.3% by weight (Example 18), 2.5% by weight (Example 19), 3.8% by weight (Example 20), and the immersions were subsequently dehydrated (pick up was 80% by weight). After the dehydration, the treated fibers were dried at 80°C for 1 hour and were treated by wet heat using a saturated steam at 120°C in an autoclave for 5 minutes to obtain fibers according to Examples 18 - 20. For the fiber according to Example 21, a fiber according to Example 14 except that wet heat was eliminated, was allocated.

**[0100]** The obtained fibers, the obtained fiber after 10 times of repeated washings and the obtained fibers as dyed were tested on absorption of unpleasant smell substances. Results of the tests and bond ratios of acid group are shown in Table 5.

(Table 5)

|            | Steam treatment | Bond ratio of acid group<br>mol% | Deodorizing characteristics of fiber   |                  | Deodorizing characteristics of fiber after 10 repetition of washing |                  | Deodorizing characteristics of fiber after dyeing |                  |
|------------|-----------------|----------------------------------|--|------------------|---|------------------|---|------------------|
|            |                 |                                  | Acetaldehyde<br>mg equivalent/kg fiber | Hydrogen sulfide | Acetaldehyde<br>mg equivalent/kg fiber                              | Hydrogen sulfide | Acetaldehyde<br>mg equivalent/kg fiber            | Hydrogen sulfide |
| Example 18 | done            | 70                               | 2.0                                    | 0.5              | 1.2   | 0.5              | 1.8   | 0.4              |
| Example 19 | done            | 81                               | 3.5                                    | 0.6              | 2.5   | 0.5              | 1.8   | 0.4              |
| Example 20 | done            | 89                               | 4.5                                    | 0.7              | 3.0   | 0.5              | 2.6   | 0.4              |
| Example 21 | none            | 45                               | 3.6                                    | 0.6              | 0.8   | 0.2              | 0.8   | 0.2              |

[0101] As shown in Table 5, the fibers according to Example 1 - 20 exhibits excellent deodorizing characteristics

towards acetaldehyde odor and hydrogen sulfide odor regarding the fibers after 10 times of repeated washing test and the dyed fiber, in comparison with the fiber according to Example 21 in which the steam treatment was omitted.

[Examples 22 - 25]

**[0102]** The never dried fiber used in Example 1 which was prepared by stretching 9 times in boiling water, was immersed at 20°C for 1 minute in aqueous solutions of polyethylene-imines differing in molecular weight at a concentration of 1% by weight; the molecular weights of polyethylene-imine are about 300 (Example 22), about 1,200 (Example 23), about 10,000 (Example 24) and about 70,000 (Example 25). The immersed fibers were dehydrated by squeezing at a pick up ratio of 100%. The dehydrated fibers were dried at 120°C for 15 minutes and subsequently wet-heat treated by a saturated steam at 120°C in an autoclave to obtain fibers according to Examples 22 - 25.

**[0103]** The fiber as obtained, the fibers after ten times of repeated washing test and the dyed fiber of the obtained fiber were tested on the offensive smell absorption test. The results obtained and bond ratios of acid groups are tabulated in Table 6.

[Table 6]

|            | Polyethylene-<br>imine<br>molecular<br>weight | Bond ratio<br>of acid<br>group<br><br>mol% | Deodorizing<br>characteristics<br>of fiber | Deodorizing<br>characteristics<br>of fiber<br>after 10 repetition<br>of washing | Deodorizing<br>characteristics<br>of fiber<br>after dyeing |
|------------|---|--|--|---|--|
|            |   |  | Acetaldehyde<br>mg equivalent/kg fiber     | Hydrogen<br>sulfide<br>mg equivalent/kg fiber                                   | Hydrogen<br>sulfide<br>mg equivalent/kg fiber              |
| Example 22 | 300   | 35   | 1.4  | 1.0   | 0.6  |
| Example 23 | 1,200   | 53   | 1.5  | 1.1   | 1.0  |
| Example 24 | 10,000  | 68   | 2.0  | 1.3   | 1.2  |
| Example 25 | 70,000  | 70   | 2.0  | 1.4   | 1.2  |
|            |   |  |  | 0.3   | 0.1  |
|            |   |  |  | 0.4   | 0.3  |
|            |   |  |  | 0.5   | 0.5  |
|            |   |  |  | 0.5   | 0.5  |

**[0104]** As shown in Table 6, the fibers according to Examples 22 - 25 which contain bonded polyethylene-imines having a molecular weight of 300 - 70,000 exhibit excellent deodorizing characteristics towards acetaldehyde and hydrogen sulfide smells even after they had been subjected to 10 times of washing test. In comparison with the fiber according to Example 22 which contains a bonded polyethylene-imine having a molecular weight of 300, the fibers according to Examples 23 - 25 which contain bonded polyethylene-imines having a molecular weight of 12,00 - 70,000 exhibit little deterioration in deodorizing characteristics towards acetaldehyde and hydrogen sulfide smells even after they were dyed.

**[Example 26]**

**[0105]** A woven fabric (weave density: 35 ends/inch, 35 picks/inch) were made from a spun yarn of 10 Nm composed of a blend fibers in which the fiber according to Example 2, Cashmilon FK (a conventional acrylic fiber available from ASAHI KASEI KOGYO KABUSHIKI KAISYA) and a fiber obtained by spinning a copolymer by copolymerizing acrylonitrile and acrylic acid in a ratio of 80 to 20 by weight in a 75% nitric acid spinning bath were blended in a mixing ratio of 3:1:6.

**[Example 27]**

**[0106]** A woven fabric was made of a blended spun yarn which was prepared by mixing a fiber according to Example 2, a transition metal-containing fiber and Cashmilon FK (an acrylic fiber available from ASAHI KASEI KOGYO KABUSHIKI KAISYA) at a mixing ratio of 3:1:6 according to the Example 26.

**[0107]** The transition metal-containing fiber was prepared by spinning a polymer obtained by copolymerizing acrylonitrile and acrylic acid in a ratio of 80 to 20 by weight into a 75% nitric acid bath, and was immersed in an aqueous solution of sodium hydroxide at a concentration of 20% by weight containing 1.5 mol/liter of sodium chloride at 20°C, and was subsequently dipped in an aqueous solution containing 10% by weight of cupric sulfate, and followed by drying after washing and dehydration.

**[Comparative Example 6]**

**[0108]** A woven fabric made of an acrylic fiber containing 0.06 mole of sulfonic acid was treated by immersing in an aqueous solution containing 12% by weight of an polyethylene-imine having a molecular weight of 70,000 at 20°C for 1 minute and was subsequently dehydrated at a pick-up ratio of 17% by weight. The treated fabric was, then, dried at 80°C for 1 hour to obtain a fiber according to Comparative Example 6.

**[0109]** The woven fabrics of Examples 29, 27 and Comparative Example 6 were evaluated on their characteristics towards various kinds of unpleasant smells in contrast to those of the fabrics after ten times of repeated washing. The results of evaluations are shown in Table 7.

**[0110]** In reference to Table 7, the fibers according to Examples 22 and 27 exhibit good characteristics with the fibers after ten times of repeated washing in comparison with those of the fiber according to Comparative Example 6. In addition, the fiber according to Examples 25 and 27 had good hand touch as shown in Table 7.

[Table 7] Residual gas concentration (ppm) in deodorizing test

|                       | Ratings of deodorizing characteristics of fiber |              |             |                  |         |                 | Hand touch rating | Tobacco smoke sensory test (Over all ratings) |
|-----------------------|---|--------------|-------------|------------------|---------|-----------------|-------------------|---|
|                       | Offensive smells                                | Acetaldehyde | Acetic acid | Hydrogen sulfide | Ammonia | Trimethyl amine |                   |   |
|                       | Initial concentration of offensive smell (ppm)  |              |             |                  |         |                 |                   |   |
| Example 26            | no washing                                      | 100          | 40          | 25               | 140     | 140             | 15                | 74  |
|                       | after 10 repetition of washing                  | 26           | 0           | 0                | 0       | 0               | 15                | 76  |
|                       | no washing                                      | 25           | 0           | 0                | 1       | 5               | 15                | 71  |
| Example 27            | after 10 repetition of washing                  | 27           | 0           | 0                | 0       | 3               | 15                | 73  |
|                       | no washing                                      | 25           | 0           | 0                | 138     | 135             | 5                 | 43  |
| Comparative Example 6 | after 10 repetition of washing                  | 88           | 35          | 23               | 129     | 131             | 10                | 25  |

[Examples 28 - 31, Comparative Example 7 - 8]

**[0111]** Woven fabrics were made of spun yarns obtained by blending the fiber obtained in Example 2, fibers prepared by immersing the never-dried fibers gathered midway during the preparation of the fiber in Example 2 into aqueous solution of polyacrylic acid so as to contain carboxyl groups at varying contents of from 0.1 mole to 15.0 mole/kg fiber and Cashimilon FK (an acrylic fiber available from ASAHI KASEI KOGYOU KABUSHIKI KAISYA), in an mixing ratio of 3:0.5:6.5.

**[0112]** The respective contents of carboxyl groups contained in the respective fibers for the respective woven fabrics are tabulated along with characteristics of the fibers towards unpleasant smells are tabulated in Table 8.

(Table 8) Residual gas concentration (ppm) in deodorizing test

| Carbonyl group content (mol/kg fiber) | Initial concentration of offensive smell (ppm) | Offensive smell |      | Acetaldehyde | Acetic acid | Hydrogen sulfide | Ammonia | Trimethyl amine | Hand touch ratings | Tobacco smoke sensory test (overall ratings) |
|---------------------------------------|--|-----------------|------|--------------|-------------|------------------|---------|-----------------|--------------------|--|
|                                       |  | washing         | none |              |             |                  |         |                 |                    |  |
| Comparative Example 7                 | 0.1  | 10 times        | 23   | 0            | 0           | 0                | 15      | 36              | 15                 | 37   |
| Example 28                            | 0.2  | 10 times        | 28   | 0            | 1           | 1                | 17      | 40              | 15                 | 41   |
| Example 29                            | 0.4  | 10 times        | 21   | 0            | 0           | 0                | 3       | 12              | 15                 | 60   |
| Example 30                            | 5.0  | 10 times        | 26   | 1            | 0           | 0                | 4       | 16              | 15                 | 62   |
| Example 31                            | 10.0   | 10 times        | 22   | 0            | 0           | 0                | 0       | 0               | 15                 | 77   |
| Comparative Example 8                 | 15.0   | 10 times        | 23   | 0            | 0           | 0                | 0       | 0               | 15                 | 76   |
|                                       |  | 10 times        | 20   | 0            | 0           | 0                | 0       | 0               | 15                 | 75   |
|                                       |  | 10 times        | 25   | 0            | 0           | 0                | 0       | 0               | 15                 | 78   |
|                                       |  | 10 times        | 21   | 0            | 0           | 0                | 0       | 0               | 15                 | 74   |
|                                       |  | 10 times        | 24   | 0            | 0           | 0                | 5       | 10              | 13                 | 63   |
|                                       |  | 10 times        | 20   | 0            | 0           | 0                | 0       | 0               | 15                 | 77   |
|                                       |  | 10 times        | 22   | 0            | 0           | 0                | 16      | 32              | 5                  | 55   |

**[0113]** Referring to Table 8, it is shown that the woven fabrics (Examples 28 - 31) made of fibers having a content of carboxyl group from 0.2 - 10 mole/kg fiber exhibit excellent deodorizing characteristics towards tobacco smells. In addition, these fibers exhibit good deodorizing fastness to washing and the fabric had good handling touch after washing.

[Examples 32 - 35, Comparative Examples 9 - 10]

**[0114]** A spinning dope containing a polymer 18% by weight was prepared by dissolving the polymer in dimethylformamide which was obtained by copolymerizing 74.7% by weight of acrylonitrile, 25.0% by weight of vinylidene chloride and sodium metharyl sulfonate. The spinning dope was extruded through a spinneret having holes having a diameter of 0.15 mm into a coagulating bath containing 75% by weight of dimethylformamide at 30°C, and was subsequently stretched 5 times in a stretching bath containing 75% by weight of dimethylformamide at 80°C and then stretched 1.2 times in a boiling water after being washed.

**[0115]** A fiber prepared from the never-dried fiber as obtained above by a method in which the never-dried fiber was immersed in an aqueous solution containing 3.8% by weight of a polyethylene-imine having a molecular weight of about 70,000 at 20°C for a period of 1 minute, dried at 80°C for 1 hour after dehydration at a pick-up ratio of 80% by weight and subsequently heat-treated by a saturated steam at 120°C in an autoclave for 5 minutes; acrylic fibers containing copper with its content varied ranging from 0.05 - 6 equivalent/kg fiber which is bonded to carboxyl group in an acrylic fiber prepared from a blend of a polymer obtained by copolymerizing acrylonitrile and acrylic acid in a copolymerizing ratio by weight of 80:20 and an polyacrylonitrile in a blending ratio of 30:70, and; a conventional polyester fiber were mixed in a blending ratio of 3:0.5:6.5 for making blended spun yarns to produce woven fabrics.

**[0116]** Deodorizing characteristic towards offensive smells for the woven fabrics were evaluated according to the manner similar to that in Example 20. Contents of copper and results of evaluation on characteristics towards offensive smells are summarized for the respective woven fabrics in Table 9.

[Table 9] Residual gas concentration in deodorizing test

|                        | Offensive smell                       |                          | Acetaldehyde | Acetic acid | Hydrogen sulfide | Ammonia | Trimethyl amine | Hand touch ratings | Tobacco smoke sensory test (overall ratings) |
|------------------------|---------------------------------------|--------------------------|--------------|-------------|------------------|---------|-----------------|--------------------|--|
|                        | Initial concentration                 | of offensive smell (ppm) |              |             |                  |         |                 |                    |  |
|                        | Copper content (equivalent/ kg fiber) |                          |              |             |                  |         |                 |                    |  |
| Comparative Example 9  | 0.05                                  |                          | 23           | 0           | 1                | 13      | 29              | 15                 | 43   |
| Example 32             | 0.1                                   |                          | 25           | 0           | 0                | 3       | 9               | 15                 | 63   |
| Example 33             | 0.2                                   |                          | 25           | 0           | 0                | 0       | 0               | 15                 | 73   |
| Example 34             | 3.0                                   |                          | 22           | 0           | 0                | 0       | 0               | 15                 | 77   |
| Example 35             | 5.0                                   |                          | 20           | 0           | 1                | 5       | 4               | 15                 | 64   |
| Comparative Example 10 | 6.0                                   |                          | 21           | 0           | 0                | 10      | 44              | 15                 | 57   |

**[0117]** In Table 9, it is shown that woven fabrics (Examples 32 - 35) made of fibers having a copper content of 0.1 - 5 equivalent/kg fiber exhibit not only deodorizing characteristics towards a carbonyl group containing compound, but also deodorizing characteristics towards a tobacco smoke smell, and that they have good hand touch.

5 [Examples 36 - 40, Comparative Examples 11 - 14]

**[0118]** 94.5% by weight of acrylonitrile, 5.0% by weight of methyl acrylate and 0.5% by weight of metharyl sulfonate were copolymerized to prepare a polymer. A spinning dope containing 15.5% by weight of the polymer was prepared by dissolving the polymer in 70% by weight aqueous nitric acid.

10 **[0119]** A never-dried fiber was prepared by spinning the spinning dope through spinneret with holes having a diameter of 0.6 mm into a nitric acid-based aqueous coagulating bath containing 75.0% by weight of nitric acid kept at a temperature of 0°C and stretch the coagulated fiber 9 times in a boiling water after washing. The never-dried fiber was immersed in an aqueous solution of a polyaryl imine having a molecular weight of about 30,000 at 25°C for 1 minute, then dried at 80°C for about 1 hour after dehydrating at a pick-up ratio of 100% by weight, and was subsequently heat  
15 treated by a saturated steam at 120°C for 5 minutes in an autoclave.

**[0120]** The obtained fiber, an acrylic acid-grafted nylon fiber in which acrylic acid was grafted so that carboxyl groups are contained in a content of 0.8 mole/kg fiber, and a conventional acrylic fiber (Cashimilon FK available from ASAHI  
20 KASEI KOGYO KABUSHIKI KAISHA) were blended in varied blending ratios to make blended spun yarns and knitted fabrics were prepared from the blended spun yarns.

**[0121]** The knitted fabrics were evaluated on their deodorizing characteristics towards offensive smells in accordance with the manners similar to those in Example 20.

**[0122]** In Table 10, the blending ratios of the acrylic fiber containing polyaryl amine and the nylon containing carboxyl groups and results of evaluation on deodorizing characteristics towards offensive smells are tabulated for the respective  
25 knitted fabrics.

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[Table 10] Residual gas concentration (ppm) in deodorizing test

|                           | Blending ratio of fiber<br>(% by weight)            |   |                                  |              | Initial concentration of offensive smell<br>(ppm) |                     |         |                    | Tobacco<br>smoke<br>sensory<br>test<br>(overall<br>ratings) |
|---------------------------|---|---|----------------------------------|--------------|---|---------------------|---------|--------------------|---|
|                           | Polyaryl<br>amine<br>containing<br>acrylic<br>fiber | Carboxyl<br>group<br>containing<br>nylon<br>fiber | Conventional<br>acrylic<br>fiber | Acetaldehyde | Acetic<br>acid                                    | Hydrogen<br>sulfide | Ammonia | Trimethyl<br>amine |   |
| Comparative<br>Example 11 | 0   | 100   | 0                                | 89           | 36  | 24                  | 0       | 0                  | 45  |
| Comparative<br>Example 12 | 1   | 99  | 0                                | 75           | 33  | 23                  | 0       | 0                  | 49  |
| Example 36                | 5   | 95  | 0                                | 40           | 26  | 19                  | 0       | 0                  | 64  |
| Example 37                | 10  | 90  | 0                                | 32           | 14  | 6                   | 0       | 0                  | 71  |
| Example 38                | 30  | 5   | 65                               | 22           | 0   | 0                   | 0       | 0                  | 77  |
| Example 39                | 99  | 1   | 0                                | 21           | 0   | 0                   | 0       | 0                  | 76  |
| Example 40                | 99.9  | 0.1   | 0                                | 20           | 0   | 0                   | 0       | 1                  | 73  |
| Comparative<br>Example 13 | 99.95   | 0.05  | 0                                | 20           | 0   | 0                   | 18      | 42                 | 56  |
| Comparative<br>Example 14 | 100   | 0   | 0                                | 19           | 0   | 0                   | 129     | 136                | 47  |

[0123] In Table 10, there are shown that knitted fabrics (Examples 36 - 40) composed of the acrylic fibers containing the polyaryl imine in a blending ratio of 5% or more by weight and the carboxyl group-containing nylon in a blending

ratio of 0.1 or more by weight deodorize not only smell of carbonyl group-containing but also smell of acid compounds and exhibit excellent deodorizing characteristics towards smell of tobacco smoke.

[Examples 41 - 45, Comparative Examples 15 - 18]

**[0124]** A polymer obtained by copolymerizing 74.7% by weight of acrylonitrile, 25% by weight of vinylidene chloride and 0.3% by weight of sodium metharyl sulfonate was dissolved in dimethylformamide to obtain a spinning dope containing 18% by weight of the polymer. The spinning dope was spun through a spinneret with holes having a size of 0.15 mm into a coagulating bath maintained at 30°C having a concentration of 75% by weight of dimethylformamide, and was then stretched 5.0 times in a stretching bath containing 75% by weight of dimethylformamide at 80°C bath, and was subsequently stretched in a boiling water after washing.

**[0125]** The fiber was treated at 25°C for 1 minute by immersing the fiber in an aqueous solution at pH 10 containing 5.0% containing 5.0% by weight of a polyaryl amine having a molecular weight of about 30,000. The immersed fiber was dehydrated at a pick-up of 100% by weight and dried at 80°C for 1 hour. The dried fiber was subsequently heat treated by a saturated steam in an autoclave at 120°C for 5 minutes.

**[0126]** The fiber obtained, an acrylic fiber containing zinc at a content of 0.2 equivalent/kg fiber which was bonded to the carboxyl group introduced by grafting acrylic acid to a conventional acrylic fiber (Cashimilon FK, available from ASAHI KASEI KOGYU KABUSHIKI KAISHA) so that carboxyl group was contained at a content of 2.0 equivalent/kg fiber, and the above-mentioned acrylic fiber (Cashimilon FK) are made into spun yarns composed of the fibers in a blending ratio of 3:0.5:6.5 to obtain woven fabrics therefrom.

**[0127]** The woven fabrics were evaluated on their deodorizing characteristics towards offensive smells in accordance with the manners described in Example 20.

**[0128]** In Table 11, the blending ratios of the acrylic fiber containing polyaryl amine and zinc-containing acrylic fiber and results of evaluation on deodorizing characteristics towards offensive smells are tabulated for the respective woven fabrics.

(Table 11) Residual gas concentration (ppm) in deodorizing test

|                           | Blending ratio of fiber<br>(% by weight)             |   |                                  | Initial concentration (ppm) of offensive<br>smell |                |                     |         |                    | Tobacco<br>smoke<br>sensory<br>test<br>(overall<br>ratings) |     |  |
|---------------------------|--|---|----------------------------------|---|----------------|---------------------|---------|--------------------|---|-----|--|
|                           | Polyaryl<br>amine-<br>containing<br>acrylic<br>fiber | Zinc-<br>containing<br>acrylic<br>fiber | Conventional<br>acrylic<br>fiber | Acetaldehyde                                      | Acetic<br>acid | Hydrogen<br>sulfide | Ammonia | Trimethyl<br>amine | 140   | 140 |  |
|                           |  |   |                                  |   |                |                     |         |                    |   |     |  |
| Comparative<br>Example 15 | 0  | 100                                     | 0                                | 86  | 33             | 22                  | 0       | 0                  | 0   | 42  |  |
| Comparative<br>Example 16 | 1  | 99                                      | 0                                | 78  | 31             | 21                  | 0       | 0                  | 0   | 46  |  |
| Example 41                | 5  | 95                                      | 0                                | 43  | 22             | 17                  | 0       | 0                  | 0   | 66  |  |
| Example 42                | 10   | 90                                      | 0                                | 30  | 16             | 3                   | 1       | 0                  | 0   | 73  |  |
| Example 43                | 30   | 5                                       | 65                               | 20  | 0              | 0                   | 1       | 2                  | 2   | 78  |  |
| Example 44                | 99   | 1                                       | 0                                | 20  | 0              | 0                   | 1       | 1                  | 1   | 75  |  |
| Example 45                | 99.9   | 0.1                                     | 0                                | 20  | 0              | 0                   | 2       | 3                  | 3   | 72  |  |
| Comparative<br>Example 17 | 95.95  | 0.05                                    | 0                                | 20  | 0              | 0                   | 18      | 34                 | 34  | 55  |  |
| Comparative<br>Example 18 | 100  | 0                                       | 0                                | 18  | 0              | 0                   | 135     | 129                | 129   | 47  |  |

**[0129]** Referring to Table 11, it is shown that woven fabrics (Examples 36 - 40) using the acrylic fibers containing the polyaryl amine in a blending ratio of 5% or more by weight and zing-containing acrylic fiber in a blending ratio of 0.1 or more by weight deodorize not only smell of carbonyl group-containing but also smell of acid compounds and exhibit excellent deodorizing characteristics towards smell of tobacco smoke.

[Example 46, Comparative Example 19]

**[0130]** A polymer obtained by copolymerizing 94.6% by weight of acrylonitrile, 5% by weight of methyl acrylate and 0.4% by weight of itaconic acid was dissolved in an aqueous nitric acid at a concentration of 70% by weight to obtain a spinning dope containing 16% by weight of the polymer. The spinning dope was spun through a spinneret with holes having a size of 0.06 mm into a nitric acid-based coagulation bath containing 35% by weight of nitric acid of which the bath temperature was maintained at 0°C, and was subsequently stretched 8 times in a boiling water after washing, and finally dried to obtain a at 80°C bath and subsequently stretched in a boiling water after washing to obtain a never-dried fiber.

**[0131]** The fiber was immersed in an aqueous solution containing a polyethylene-imine having a molecular weight of about 70,000 at a concentration of 2.5% by weight at 20°C for 1 minute, and dried at 80°C for 1 hour after dehydration at a pickup ratio of 80% by weight, and subsequently heat treated by wet heating by a saturated steam at 120°C for a period of 5 minutes in an autoclave to obtain a treated fiber.

**[0132]** A woven fabric (Example 46) was prepared using a blended spun yarn prepared by blending the above-mentioned fiber, a fiber which was prepared from a blended polymer composition by blending a polymer obtained by copolymerizing acrylonitrile and acrylic acid at a mixing ratio of 80:200 and polyacrylonitrile at a blending ratio of 80:70, and a conventional acrylic fiber at a blending ratio of 3:1:6.

**[0133]** Another woven fabric was prepared for Comparative Example 19 in which the fabric was obtained according to the same manner and conditions as those in Example 46 except that the heat treatment by wet heat was omitted.

**[0134]** For the Example and Comparative Example, evaluations of deodorizing characteristic toward offensive smells were carried out on the woven fabrics prepared, the woven fabric subsequent to ten times of repeated washing tests and the woven fabric subsequent to dyeing.

**[0135]** The results of the evaluations are tabulated in Table 12.

[Table 12] Residual gas concentration (ppm) in deodorizing test

|                        | Bond ratio of acid group mol% | Ratings of deodorizing characteristics |              |             |                  |         |                 | Tobacco smoke sensory test (overall ratings) |
|------------------------|-------------------------------|--|--------------|-------------|------------------|---------|-----------------|--|
|                        |                               | Offensive smell                        | Acetaldehyde | Acetic acid | Hydrogen sulfide | Ammonia | Trimethyl amine |  |
|                        |                               | Initial concentration (ppm)            |              |             |                  |         |                 |  |
| Example 46             | 81                            | No washing                             | 22           | 0           | 0                | 0       | 0               | 74   |
|                        |                               | Washing 10 times                       | 26           | 0           | 0                | 0       | 0               | 76   |
|                        |                               | After dyeing                           | 32           | 1           | 0                | 1       | 0               | 72   |
|                        |                               | No washing                             | 25           | 0           | 0                | 1       | 0               | 73   |
| Comparative Example 19 | 45                            | Washing 10 times                       | 76           | 35          | 1                | 0       | 0               | 55   |
|                        |                               | After dyeing                           | 69           | 38          | 0                | 1       | 0               | 48   |

[0136] In Table 12, it is apparent that an acrylic fiber in which a bond ratio of acid group to polyethylene-imine was made 50 mol/kg fiber or more by applying wet heat treatment in the treatment step of the undried acrylic fiber with a polyethylene-imine, exhibits good deodorizing characteristics towards smells of carbonyl group-containing compounds and acid compounds on the fiber after 10 times of repetition of washing and the fiber after dyeing.

#### Industrial Applicability

[0137] The deodorizing fiber according to the invention have a deodorizing characteristics capable of removing of-fensive smells originating from acid compounds such as carbonyl compounds by adsorption. The deodorizing characteristics of fiber do not deteriorate during textile processing such as dyeing or the like after a number of repeated washing. As a raw material fiber for woven and knitted fabric, the deodorizing fiber of the invention can provide a variety of textile articles covering clothing and interior and furnishings with fast deodorizing characteristics.

[0138] Textile converted articles made from a mixture of the deodorizing fiber of the invention with a deodorizing fiber having an anionic functional group in the fiber substrate which is capable of removing offensive smells emitted from a basic compound, can remove a compound smell in which a basic and an acid compounds are involved, and the deodorizing characteristics of the articles are durable.

[0139] with the use of a fiber of the invention as a component of a blend, a textile article can exhibit a fast deodorizing effect on a compound smell, for an example, tobacco smoke smell in which various smells are involved.

#### Claims

1. A deodorizing fiber composed of a substrate fiber containing carboxylic or sulphonic acid groups in an amount of 0.01-2.5 mol/kg fiber and a polyamine compound with a molecular weight of 1,000 - 200,000 being deposited on said substrate fiber to provide an amount of amino groups of 0.03-3 mol/kg fiber and where a part of said amino groups are bonded ionically to at least a part of said acid groups and wherein the deodorizing fiber exhibits free amino groups.
2. A deodorizing fiber according to claim 1 wherein 50-100 mol% of the acid groups are ionically bonded to amino groups of the polyamine compound.
3. A deodorizing fiber according to claim 1, **characterized in that** the fiber substrate is an acrylic fiber.
4. A process for producing a deodorizing fiber according to claim 1 wherein a fiber containing acid groups selected from the group consisting of carboxylic acid and sulfonic acid in an amount of 0.01 - 2.5 mol/kg fiber is impregnated with a solution of a water-soluble polyamine compound having a molecular weight of 1,000 - 200,000 so that the fiber contains the polyamine compound in an amount of 0.03 - 3 mol/kg fiber in terms of the amino groups thereof, and that the impregnated fiber is subsequently heat treated to fix the polyamine compound to the fiber by bonding it ionically to the acid group so as to maintain the presence of free amino groups in the fiber.
5. A process according to claim 4, **characterized in that** the fiber substrate is an acrylic fiber.
6. A process according to claim 4 or 5 wherein acrylic fiber containing acid groups selected from the group consisting of carboxylic acid and sulfonic acid in the fiber substrate at an amount of 0.01 - 2.5 mol/kg fiber in which a never-dried acrylic fiber is in its aqueous swollen state which is before the fiber structure becomes irreversibly densified by drying and has an initial swelling degree (Qc) of 50 - 250 % by weight, is contacted with a solution of a water-soluble polyamine compound having a molecular weight of 1,000 - 200,000 so that the fiber contains the water-soluble polyamine compound in an amount of 0.03 - 3 mol/kg fiber in terms of the amino groups thereof, and that the impregnated fiber is subsequently heat treated to fix the polyamine compound to the fiber by binding amino groups ionically to acid groups, wherein Qc (%) is defined as  $(W_1 - W_2)/W_2 \times 100$  ( $W_1$  represents a weighing (g) of a specimen weighing several grams of a fiber which has never been dried, centrifuged at 900 G at 25 °C for 5 minutes and  $W_2$  represents weighing of the specimen after drying at 105 °C for 2 hours).
7. A textile article having deodorizing characteristics comprising at least 5 % by weight of a deodorizing fiber (A) as defined in any one of claims 1 to 3 and at least 0.1 % by weight of a deodorizing fiber (B) containing either an anionic functional group in the fiber substrate in an amount of 0.2 - 10 equivalent/kg fiber, or transition metal bonded to anionic functional groups in an amount of 0.2 - 10 equivalent/kg fiber as blended components.

8. A textile article according to claim 7, wherein the transition metal is copper or zinc.
9. A textile article according to any one of claims 7 or 8 wherein the deodorizing fiber (A) is an acrylic fiber substrate according to claim 1.

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### Patentansprüche

- 10 1. Desodorisierende Faser, die aus einer Substratfaser besteht, die Carbonoder Sulfonsäuregruppen in einer Menge von 0,01 bis 2,5 mol/kg Faser enthält, wobei eine Polyaminverbindung mit einem Molekulargewicht von 1000 bis 200 000 auf der Substratfaser abgeschieden ist, so dass man eine Menge an Aminogruppen von 0,03 bis 3 mol/kg Faser erhält, wobei ein Teil der Aminogruppen ionisch an wenigstens einen Teil der Säuregruppen gebunden sind und wobei die desodorisierende Faser freie Aminogruppen aufweist.
- 15 2. Desodorisierende Faser gemäß Anspruch 1, wobei 50 bis 100 Mol-% der Säuregruppen ionisch an Aminogruppen der Polyaminverbindung gebunden sind.
3. Desodorisierende Faser gemäß Anspruch 1, **dadurch gekennzeichnet, dass** das Fasersubstrat eine Acrylfaser ist.
- 20 4. Verfahren zur Herstellung einer desodorisierenden Faser gemäß Anspruch 1, wobei eine Faser, die Säuregruppen, die aus der Gruppe ausgewählt sind, die aus Carbonsäure und Sulfonsäure besteht, in einer Menge von 0,01 bis 2,5 mol/kg Faser enthält, mit einer Lösung einer wasserlöslichen Polyaminverbindung mit einem Molekulargewicht von 1000 bis 200 000 imprägniert wird, so dass die Faser die Polyaminverbindung in einer Menge von 0,03 bis 3 mol/kg Faser enthält, bezogen auf die darin enthaltenen Aminogruppen, und wobei die imprägnierte Faser anschließend wärmebehandelt wird, so dass die Polyaminverbindung auf der Faser fixiert wird, indem sie ionisch an die Säuregruppen gebunden wird, so dass die Anwesenheit von freien Aminogruppen in der Faser aufrechterhalten wird.
- 25 5. Verfahren gemäß Anspruch 4, **dadurch gekennzeichnet, dass** das Fasersubstrat eine Acrylfaser ist.
- 30 6. Verfahren gemäß Anspruch 4 oder 5, wobei eine Acrylfaser, die Säuregruppen, die aus der Gruppe ausgewählt sind, die aus Carbonsäure und Sulfonsäure besteht, in dem Fasersubstrat in einer Menge von 0,01 bis 2,5 mol/kg Faser enthält, wobei sich eine noch nie getrocknete Acrylfaser in ihrem wässrigen aufgequellten Zustand befindet, d.h. bevor die Faserstruktur durch Trocknen irreversibel verdichtet wird, und einen Anfangsquellgrad ( $Q_c$ ) von 50 bis 250 Gew.-% aufweist, mit einer Lösung einer wasserlöslichen Polyaminverbindung mit einem Molekulargewicht von 1000 bis 200 000 in Kontakt gebracht wird, so dass die Faser die wasserlösliche Polyaminverbindung in einer Menge von 0,03 bis 3 mol/kg Faser enthält, bezogen auf die darin enthaltenen Aminogruppen, und wobei die imprägnierte Faser anschließend wärmebehandelt wird, so dass die Polyaminverbindung auf der Faser fixiert wird, indem Aminogruppen ionisch an Säuregruppen gebunden werden, wobei  $Q_c$  (%) als  $(W_1 - W_2)/W_2 \times 100$  definiert ist (wobei  $W_1$  das Gewicht (g) einer mehrere Gramm wiegenden Probe einer noch nie getrockneten Faser darstellt, die 5 Minuten lang bei 25 °C mit  $900 \times g$  zentrifugiert wurde, und  $W_2$  das Gewicht der Probe nach 2 Stunden Trocknen bei 105 °C darstellt).
- 35 7. Textilartikel mit desodorisierenden Eigenschaften, der wenigstens 5 Gew.-% einer desodorisierenden Faser (A) gemäß einem der Ansprüche 1 bis 3 und wenigstens 0,1 Gew.-% einer desodorisierenden Faser (B), die entweder eine anionische funktionelle Gruppe im Fasersubstrat in einer Menge von 0,2 bis 10 Äquivalenten/kg Faser oder an anionische funktionelle Gruppen gebundenes Übergangsmetall in einer Menge von 0,2 bis 10 Äquivalenten/kg Faser enthält, als gemischte Komponenten umfasst.
- 40 8. Textilartikel gemäß Anspruch 7, wobei das Übergangsmetall Kupfer oder Zink ist.
- 45 9. Textilartikel gemäß einem der Ansprüche 7 oder 8, wobei die desodorisierende Faser (A) ein Acrylfasersubstrat gemäß Anspruch 1 ist.
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## Revendications

1. Fibre désodorisante composée d'une fibre servant de substrat et contenant des groupes acide carboxylique ou sulfonique en une quantité de 0,01 à 2,5 moles/kg et d'un composé de polyamine d'un poids moléculaire de 1 000 à 200 000 déposé sur la fibre servant de substrat pour donner une quantité de groupes amino de 0,03 à 3 moles/kg de fibre, une partie des groupes amino étant liée ioniquement à au moins une partie des groupes acide et la fibre désodorisante ayant des groupes amino libres.
2. Fibre désodorisante selon la revendication 1, dans laquelle de 50 à 100 % en moles des groupes acide sont liés ioniquement aux groupes amino du composé de polyamine.
3. Fibre désodorisante suivant la revendication 1, **caractérisée en ce que** le substrat de la fibre est une fibre acrylique.
4. Procédé de production d'une fibre désodorisante suivant la revendication 1, dans lequel une fibre contenant un groupe acide choisi dans le groupe consistant en l'acide carboxylique et l'acide sulfonique en une quantité de 0,01 à 2,5 moles/kg de fibre est imprégnée d'une solution d'un composé de polyamine soluble dans l'eau ayant une masse moléculaire de 1 000 à 200 000 de sorte que la fibre contient le composé de polyamine en une quantité de 0,03 à 3 moles/kg de fibre en termes de ses groupes amino et en ce que la fibre imprégnée est ensuite traitée thermiquement pour fixer le composé de polyamine à la fibre en le liant ioniquement au groupe acide de manière à maintenir la présence de groupes amino libres dans la fibre.
5. Procédé suivant la revendication 4, **caractérisé en ce que** le substrat de la fibre est une fibre acrylique.
6. Procédé suivant la revendication 4 ou 5, dans lequel la fibre acrylique contenant un groupe acide sélectionné dans le groupe consistant en l'acide carboxylique et l'acide sulfonique dans le substrat de la fibre en une quantité de 0,01 à 2,5 moles/kg de fibre, dans lequel une fibre acrylique qui n'a jamais été séchée et qui est dans son état aqueux gonflé qui est celui avant que la structure de la fibre devienne densifiée d'une manière irréversible par séchage et a un degré initial de gonflement ( $Q_c$ ) de 50 à 250 % en poids, est mise en contact avec une solution d'un composé de polyamine soluble dans l'eau d'un poids moléculaire de 1 000 à 200 000 de façon à ce que la fibre contienne le composé de polyamine soluble dans l'eau en une quantité de 0,03 à 3 moles/kg de fibre en termes de ses groupes amino, et en ce que la fibre imprégnée est ensuite traitée thermiquement pour fixer le composé de polyamine à la fibre en liant des groupes amino ioniquement aux groupes acide,  $Q_c$  (%) étant défini par  $(W_1 - W_2)/W_2 \times 100$  ( $W_1$  représentant un poids (g) d'un échantillon pesant plusieurs grammes d'une fibre qui n'a jamais été séchée, centrifugée à 900 G à 25°C pendant 5 minutes,  $W_2$  représentant le poids de l'échantillon après séchage à 105°C pendant 2 heures).
7. Article textile ayant des caractéristiques désodorisantes comprenant au moins 5 % d'une fibre (A) désodorisante telle que définie dans l'une quelconque des revendications 1 à 3, et au moins 0,1 % en poids d'une fibre (B) désodorisante contenant soit un groupe fonctionnel anionique dans le substrat de la fibre en une quantité de 0,2 à 10 équivalents/kg de fibre, soit un métal de transition lié à des groupes fonctionnels anioniques en une quantité de 0,2 à 10 équivalents/kg sous forme de constituants mélangés.
8. Article textile suivant la revendication 7, dans lequel le métal de transition est le cuivre ou le zinc.
9. Article textile suivant l'une quelconque des revendications 7 ou 8, dans lequel la fibre (A) désodorisante est un substrat de fibre acrylique suivant la revendication 1.